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PCT

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>5</sup> : G03F 7/004, C23C 16/18 H01L 21/285, G03F 1/08, 7/16 G03F 7/20, C07F 1/12</p>	A1	<p>(11) International Publication Number: WO 94/11787 (43) International Publication Date: 26 May 1994 (26.05.94)</p>
<p>(21) International Application Number: PCT/GB93/02391 (22) International Filing Date: 19 November 1993 (19.11.93)  (30) Priority data: 9224233.8 19 November 1992 (19.11.92) GB 9306446.7 27 March 1993 (27.03.93) GB 9317750.9 26 August 1993 (26.08.93) GB  (71) Applicant (for all designated States except US): THE UNIVERSITY COURT OF THE UNIVERSITY OF DUNDEE [GB/GB]; Dundee DD1 4HN (GB).  (72) Inventors; and (75) Inventors/Applicants (for US only): THOMSON, James [GB/GB]; CAIRNS, James [GB/GB]; The University Court of The University of Dundee, Dundee DD1 4HN (GB).</p>		<p>(74) Agent: PATTULLO, Norman; Murgitroyd and Company, 373 Scotland Street, Glasgow G5 8QA (GB).  (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: METHOD OF DEPOSITION</p> <p>(57) Abstract</p> <p>There is described a method of chemically depositing a substance. The method is of utility in the direct manufacture of integrated circuits and in the manufacture of a photomask for use in production of integrated circuits. The method involves the use of a compound which degrades into a deposit and a residue when a radiant beam (e.g. a laser beam) or a particle beam (e.g. an electron beam) is applied. The residue and any unreacted compound may be washed off the substrate to which it has been applied. Nanoscale dimensions of the deposit can be achieved. A particularly suitable organometallic compound is tetra-sec butyl di-aurum difluoride.</p> <div style="position: absolute; bottom: 50px; left: 50px; transform: rotate(-45deg); font-family: cursive; font-size: 1.2em;"><p>US PN 5821017 61071676 EP 0670 055B1</p></div>		

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1     "Method of Deposition"

2

3     This invention relates to a method of depositing  
4     substances, for example metals. The method may be used  
5     in the manufacture of integrated circuits and  
6     photomasks.

7

8     Modern technological demands in integrated circuitry,  
9     for example opto-electronics and electronic surgical  
10    implants, now require methods by which ultra fine metal  
11    lines of submicron dimensions can be deposited onto  
12    inert substrate materials. There is a considerable  
13    demand for submicron technology in a wide variety of  
14    disciplines, but there are many difficulties in  
15    developing nanoscale metal deposition processes by  
16    conventional lithographic methods. Lithography is the  
17    process by which a pattern is transferred to the  
18    surface of a substrate material. Before this process  
19    can occur a photomask has to be prepared which defines  
20    the pattern ultimately to be achieved on the substrate  
21    layer.

22

23    Conventionally the photomasks required in the  
24    manufacture of integrated circuits are made by applying  
25    a film layer of metal, usually chromium since this

1 resists scratching or etching and has good adhesion  
2 properties, by metal vapour deposition to a highly pure  
3 quartz substrate which has been polished to give an  
4 extremely flat surface. The exposed metal is then  
5 covered with electron beam resist (which is a material  
6 that is sensitive to a beam of electrons and is  
7 disrupted on exposure thereto) by placing a drop of  
8 resist in the middle of a spinning disk of mask  
9 material. The resist is then baked and dried in an  
10 oven. The usual electron beam resist is  
11 polybutylsulphone (PBS).

12  
13 An electron beam is directed at the resist face of the  
14 resist/metal/substrate composite to degrade portions of  
15 the resist, leaving unaffected a pattern required for  
16 the integrated circuit. The degraded resist is then  
17 dissolved away using a proprietary etchant to expose  
18 the layer of metal in the areas where the resist has  
19 been degraded, and this is subjected to wet etching by  
20 ceric ammonium nitrate to remove the metal and expose  
21 the quartz substrate. The remaining resist is then  
22 burnt off from the residual metal, resulting in a  
23 product through which light can pass apart from the  
24 areas masked by metal.

25  
26 The photomask thus produced is used to define a pattern  
27 on a silicon chip coated with photoresist, by passing  
28 ultraviolet light through the photomask to degrade the  
29 photoresist in the defined areas.

30  
31 This method of manufacturing photomasks has a number of  
32 disadvantages. For example, the dissolution of the  
33 degraded photoresist may not be entirely uniform, and  
34 while the result is adequate for many products current  
35 computer technology demands increasingly dense patterns

1 on integrated circuits and therefore higher-definition  
2 photomasks, down to the nanoscale level.

3  
4 A further area of loss of definition is the wet etch  
5 process for removing the unwanted chromium. The etch  
6 material attacks the upper, exposed face of the  
7 chromium but as it penetrates into the chromium layer  
8 its effect is not unidirectional, so instead of  
9 producing vertical walls for the residual chromium it  
10 erodes and undercuts these walls. This can produce a  
11 scattering effect on the ultraviolet light during  
12 manufacture of the integrated circuits, reducing  
13 definition of the applied pattern. This is one of the  
14 principal problems in mask-making.

15  
16 Where several photomasks are used successively in the  
17 manufacture of a chip, accurate registration of each  
18 mask is absolutely essential so that each feature  
19 appears in the correct place on the finished chip.  
20 Problems in epitaxy can cause pattern shift and thus  
21 registration. Usually registration is accurate to +/-  
22 0.2 $\mu$ m. Registration problems, epitaxy growth problems,  
23 undercutting, constructive and destructive interference  
24 during lithographic process at micron and submicron  
25 dimensions, all contrive to indicate that mask-making  
26 at nanometer dimensions may require an entirely new  
27 manufacturing process.

28  
29 For nanoscale circuits, conventional methods using  
30 metallic inks do not as yet possess the specifications  
31 which can ensure the deposition of accurate straight  
32 lines of high specification, and the formation of  
33 perfect right angles rather than arcs during integrated  
34 circuit manufacture. The low specification of the  
35 conventional process of metallisation can result in

1 circuit overlap and circuit breakage which cannot be  
2 tolerated when scribing nanoscale circuits. Further,  
3 when ultra fine lines are required to carry current it  
4 is a fundamental requirement that the circuit-integrity  
5 remains intact, and hence conductive materials which  
6 are oxidized are not ideally suited to operate at such  
7 dimensions.

8  
9 According to the present invention there is provided a  
10 method of chemical deposition comprising applying to a  
11 substrate a compound which degrades under the effect of  
12 a radiant or particle beam to produce a deposit,  
13 applying to selected surface areas of said compound  
14 such a radiant or particle beam and removing the  
15 degraded compound and the unaffected compound from the  
16 substrate. The deposit is left upon the substrate.

17  
18 The process of the present invention causes degradation  
19 of the compound only where contacted by the radiant or  
20 particle beam. In other words, the dimensions of the  
21 deposit caused by degradation of the compound is  
22 proportional to the focal width of the irradiating  
23 beam. Nanoscale dimensions may be achieved by the  
24 process of the present invention.

25  
26 Where the compound degrades to form a deposit of a  
27 metallic or other conductive substance, then the method  
28 may be used to manufacture integrated circuits directly  
29 on the substrate. The deposit is preferably a metal or  
30 metal alloy, and mention may be made of metals such as  
31 gold, tin and chromium, or the deposit may be a  
32 conductive non-metal or semi-metal, such as germanium.

33  
34 In a further aspect there is provided a method of  
35 manufacture of an integrated circuit, said method

1 comprising applying to a substrate a compound which  
2 degrades under the effect of a radiant or particle beam  
3 to produce a conductive, preferably metallic deposit,  
4 applying to selected surface areas of said compound  
5 such a radiant or particle beam and removing the  
6 degraded compound and the unaffected compound from the  
7 substrate.

8

9 Alternatively, the method of the present invention may  
10 be used to manufacture a photomask which is then  
11 subsequently used in lithography to manufacture  
12 integrated circuits. In this embodiment the substrate  
13 should be translucent or transparent and the deposit  
14 formed by degradation of the compound should be opaque.  
15 The deposit provides a barrier to passage of  
16 ultraviolet light during use of the photomask in making  
17 integrated circuits, as with the chromium in  
18 conventional photomasks.

19

20 Thus in a yet further aspect, the present invention  
21 provides a method of manufacture of a photomask, said  
22 method comprising applying to a transparent or  
23 translucent substrate a compound which degrades under  
24 the effect of a radiant or particle beam to produce an  
25 opaque deposit, applying to selected surface areas of  
26 said compound such a radiant or particle beam and  
27 removing the degraded compound and the unaffected  
28 compound from the substrate.

29

30 In this embodiment the deposit formed by the action of  
31 the particle or radiant beam need only be opaque and  
32 there is no requirement for the deposit to be  
33 conductive. Therefore the deposit may be of any  
34 suitable opaque material, whether metal or non-metal.  
35 The opaque deposit may be for example a metal or semi-



1 metal such as gold, tin, germanium or chromium, an  
2 alloy, or a non-metal such as silicon or carbon.

3

4 In the present invention, the compound may be heat-  
5 sensitive so that the use of a radiant beam in the form  
6 of a laser beam degrades the compound to produce the  
7 deposit.

8

9 Preferably, however, the particle beam is an electron  
10 beam, in which case the compound may be for example an  
11 organometallic compound which degrades under the effect  
12 of the beam to deposit a metal on the substrate.

13

14 Conventionally the steric properties of the  
15 organometallic material which may be used as the  
16 compound in the process of invention are optimised by  
17 selecting  $d^8$  configurations which give square planar  
18 geometry in the organometallic compound. Such  
19 compounds include organometallic gold, platinum or  
20 palladium fluorides.

21

22 In a yet further aspect, the present invention provides  
23 a gold organometallic fluoride. Optionally the gold  
24 organometallic fluoride may be used in the method of  
25 deposition described herein.

26

27 Gold is an especially useful metal for inclusion in an  
28 organometallic compound to be used in the method of  
29 this invention, and a suitable organometallic form is  
30 di-sec butylaurum (III) fluoride dimer.

31

32 Gold chemistry exists mainly in the Au(I) and Au(III)  
33 oxidation states. Inorganic gold compounds usually  
34 have the linear 2 co-ordination state and occasionally  
35 exist in trigonal planar or tetrahedral configurations.

1 Au(III) compounds are in general square planar but can  
 2 exist in five or six coordinated states. Simple  
 3 organogold compounds ( $\text{AuR}$  - where R is any organic  
 4 group) have not as yet been found although adduct  
 5 compounds of Au(I) with phosphines or isocyanides are  
 6 known. Trigonal planar Au(I) organoaurates (eg  
 7  $\text{Li}[\text{AuCH}_3]_2$ ) exhibit low stability, spontaneously  
 8 decomposing by reductive elimination of the methyl  
 9 groups to give ethane. The trigonal planar gold  
 10 complexes gain stability if complexed with larger  
 11 ligands (eg  $\text{Li}(\text{PMDT})[\text{AuCH}_3]_2$ , where PMDT = pentamethyl-  
 12 diethylenetrisamine)

13  
 14 Au(I) organyls are also accessible through carbene  
 15 insertion into the Au-Cl bond.

16

17 eg  $(\text{C}_2\text{H}_5)_3\text{PAuCl} + \text{CH}_2\text{N}_2 \text{ -----} (\text{C}_2\text{H}_5)_3\text{PAuCl} + \text{N}_2$

18

19 Au(III) organyls also require additional ligation to  
 20 provide stability. Square planar compounds are  
 21 obtained eg:  $(\text{C}_6\text{F}_5)_2\text{AuClPPh}_3$ . Halogen bridging Au  
 22 complexes are known through the auration reaction:

23

24 eg:  $2\text{Au}_2\text{Cl}_6 + 2\text{C}_6\text{H}_5 \text{ -----} \text{C}_6\text{H}_5\text{.Cl.Au.Cl.Cl.Au.Cl.C}_6\text{H}_5$

25

26 Other typical organometallic compounds for use in this  
 27 invention are polyalkyl metal fluorides, for example  
 28 polydibutyltin difluoride, as these compounds contain  
 29 generally linear chains which allow good definition of  
 30 the affected areas of the compound on application of  
 31 the radiant or particle beam.

32

33 The organometallic compounds are advantageously  
 34 fluorides since the fluoride component enhances the  
 35 adhesion between the substrate (such as silicon or

1 quartz) and the metal film formed after irradiation.  
2 The enhanced adhesive is believed to be due to the  
3 formation of Si-F bonds. This enhanced adhesion is not  
4 achieved with the equivalent chloride and bromide  
5 compounds. Particularly good adhesion is observed when  
6 tetra-sec-butyldiaurum difluoride is used as the  
7 organometallic compound. A further advantage is that an  
8 especially even dispersion of organometallic compound  
9 is observed where a fluoride compound is used.

10

11 Fluorine bridging in organogold complexes has not been  
12 reported but pentafluorochalcogenate derivatives of  
13 gold are known (ie  $\text{Au}(\text{OTeF}_5)_3$ ). The group  $\text{OTeF}_5$  is often  
14 regarded as a pseudohalogen but more precisely is a  
15 pseudofluorine. The ability of Au to form bridging  
16 species renders the gold pentafluorochalcogenate  
17 compound the only known binary transition metal  
18 derivative of  $\text{OTeF}_5$ . This compound is of a  
19 centrosymmetric dimer with four terminal  $\text{TeF}_5$  groups and  
20 two  $\mu$ -oxo bridging bidentate  $\text{OTeF}_5$  groups

21

22 Further according to the invention there is provided a  
23 method of preparing polydibutyltin difluoride,  
24 comprising fluorinating polydibutyltin dichloride.

25

26 Polydibutyltin dichloride is commercially available but  
27 is unstable at ambient temperature. The difluoride,  
28 while known, has until now been very difficult to  
29 produce.

30

31 The fluorination may be carried out using for example  
32 sodium fluoride, and the resulting polydibutyltin  
33 difluoride may be used in the manufacture of photomasks  
34 by applying it, for example by spinning, to a  
35 transparent or translucent substrate such as quartz.

1 In this process the quartz is rapidly rotated while the  
2 polydibutyltin difluoride in solution is slowly  
3 applied, for example by drip, to it. The solvent is  
4 then driven off leaving an accurately-controlled layer  
5 of the organometallic compound.

6  
7 In some cases it is possible to deposit the opaque  
8 material by application to the substrate of a solution  
9 of the degradable compound and then driving off the  
10 solvent, preferably by microwave heating which has the  
11 effect of allowing the solvent to be removed from the  
12 substrate interface early in the procedure, thereby  
13 producing effective adhesion between the deposited  
14 degradable compound and the substrate.

15  
16 In investigating the yield of organometallic precursor  
17 material extracted from the reactant mixture as a  
18 function of solvent polarity, cyclohexane, n-hexane,  
19 isopentane, chlorofluorocarbon 113 ( $\text{CCl}_2\text{FCClF}_2$ ), CFC-  
20 113a ( $\text{CCl}_2\text{CF}_3$ ), n-pentane and iso-pentane have been  
21 examined. The optimum solvent to provide a smooth even  
22 distribution of organometallic material on a quartz  
23 substrate was found to be a low-boiling-point aliphatic  
24 hydrocarbon solvent. Hence, n-pentane or isopentane  
25 are excellent solvents for work to be performed at  
26 ambient temperatures.

27  
28 Embodiments of the present invention will now be  
29 described by way of illustration in the following  
30 Examples.

31  
32  
33

1     Example 1

2

3     Preparation of Polydibutyltin difluoride

4

5     Analar grade methanol (50ml, B.D.H.) was transferred to  
6     a conical flask containing 2.1g of dried sodium  
7     fluoride (Aldrich Chemical Co.,). The flask was shaken  
8     to dissolve the solid material. Dibutyltin dichloride  
9     (0.5g, Aldrich Chemical Co.,) was added and the conical  
10    flask was stoppered and sealed using paraffin film.  
11    The system was shaken for 1 hour, then allowed to stand  
12    for 12 hours at ambient temperature.

13

14    The reaction mixture was then passed through a sintered  
15    glass filter to remove any undissolved sodium fluoride  
16    prior to the eluent being transferred to a phase  
17    separation vessel. Petroleum ether (bp. 60-80°C, 100  
18    ml) was added to the eluent phase and the reaction  
19    mixture shaken before allowing the mixture to settle  
20    and separate. Using the upper phase, the purification  
21    process was repeated a further three times using  
22    methanol (100ml) before the upper phase was finally  
23    transferred to a 250 ml round bottom flask. The flask  
24    containing the reaction solution was affixed to a  
25    rotary evaporator and allowed to evaporate down until a  
26    precipitate appeared.

27

28    The solution was analysed by Raman Spectroscopy and  
29    identified as a low molecular weight polymer of  
30    dibutyltin difluoride.

31

32    Application and Preparation of Organometallic Overlayer

33

34    The solution of polydibutyltin difluoride monomer  
35    prepared above was spun onto a clean polished quartz

1 plate. As the solvent evaporated off a film of  
2 polymeric dibutyltin difluoride formed on the quartz  
3 substrate. The organometallic overlayer supported on  
4 the quartz substrate was placed in a JEOL T300 Scanning  
5 Electron Microscope and bombarded with electrons  
6 (energy 30 keV) for a time which varied from 5s to 10  
7 min over an area of 100 x 100  $\mu\text{m}$ . of the organometallic  
8 sample, then moved to an adjacent area.

9  
10 After irradiation of each area the sample was examined  
11 using an optical microscope to reveal a linear track of  
12 metallic particles, approx. 10  $\mu\text{m}$  wide. The non-  
13 degraded polydibutyltin difluoride film was removed by  
14 dissolution in methanol.

15  
16 Using the method of this embodiment it is possible to  
17 produce a photomask of very high definition so that  
18 dense and discrete patterns can be applied to silicon  
19 chips to provide integrated circuits. The method  
20 removes the need for affected electron beam resist to  
21 be dissolved as in the conventional method, and also  
22 for the wet etch process, both of which reduce the  
23 definition and performance of the photomask.

24  
25 Example 2

26  
27 Preparation of Di-sec butylaurum (III) Fluoride dimer.

28  
29 Magnesium turnings were degreased by washing in sodium  
30 dried ether and transferred to a double-necked round  
31 bottom flask containing a magnetic stirring bar.  
32 Sufficient sodium dried ether was added to cover the  
33 magnesium turnings. The flask was fitted with a water  
34 cooled condenser and a dropping funnel charged with  
35 5.62g dibutyl bromide (Aldrich Chemical Co.) in 80ml of

1 sodium dried ether. The butylbromide/. ether mixture  
2 was added slowly and allowed to react with stirring  
3 with the magnesium turnings. The system was left to  
4 react for 2 hours at ambient temperature.

5  
6 The prepared butyl magnesium bromide/ether mixture was  
7 decanted to a dry dropping vessel and fitted to a  
8 double necked roundbottom flask containing an ethereal  
9 solution of aurum (III) chloride (500mg in 20ml ether  
10 Aldrich Chemical Co) cooled with powdered ice. The  
11 ethereal solution of butyl magnesium bromide was added  
12 slowly with stirring to the aurum (III) chloride  
13 solution over a 20 minute period. After reaction  
14 powdered ice was added to the reactant mixture which  
15 was then allowed to warm up to ambient temperature.

16  
17 The resultant organometallic gold halide was extracted  
18 from the reactant mixture using isopentane in a phase  
19 separation process. A dry methanol/isopentane phase  
20 separation process was performed a further three times.  
21 The product mixture was reacted with sodium fluoride  
22 (Aldrich Chemical Co, 2.1g) dissolved in 50ml of dried  
23 methanol (BDH), and shaken at ambient temperature over  
24 a 24 hour period. The mixture was then passed through  
25 a sintered glass filter to remove any undissolved NaF  
26 prior to the eluent being transferred to a phase  
27 separation vessel. Three phase separation cycles were  
28 performed using an isopentane/dry methanol mixture  
29 containing the reaction products, the hydrocarbon phase  
30 being carried over in each step of the separations.  
31 The final hydrocarbon phase was transferred to a round  
32 bottom flask, affixed to a rotary evaporator, and  
33 allowed to evaporate down until a precipitate appeared.  
34 The product material had a white waxy appearance and  
35 gave off a pungent odour. Contact of the product

1 material with the skin left a purple stain consistent  
2 with the deposition of colloidal gold.

3  
4 Characterisation of the product material was performed  
5 using  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and Distortionless Enhancement by  
6 Polarization Transfer (DEPT) liquid phase NMR (nuclear  
7 magnetic resonance) analysis using  $\text{CDCl}_3$  or  
8 deuterobenzene as solvent (Figures 1-5). Mass  
9 spectroscopy was also used to identify the product  
10 material (Figures 6-7).

11

12 Results:

13

14  $^1\text{H}$  NMR analysis of the product material gave peaks at  
15 1.38 (hextet), 1.13 (hextet) and 0.79 (d of d) (Figures  
16 1 and 1a). Two dimensional  $^1\text{H}$  analysis of the material  
17 shows three proton environments (Figure 2) and DEPT  
18 analysis shows that the proton arrangement on the  
19 organic liquid is one carbon containing an even number  
20 of protons and three carbons containing an odd number  
21 of protons (Figure 4).  $^{13}\text{C}$  NMR analysis (Figure 3) of  
22 the product material shows 4 peaks at 31.5, 29.7, 22.2,  
23 11.7 ppm relative to TMS. The data indicates that four  
24 carbon environments are present in the product  
25 material.  $^{19}\text{F}$  NMR analysis of the product material  
26 (proton coupled and proton decoupled spectra) shows a  
27 singlet peak at -66.3 ppm confirming the presence of  
28 fluorine in the product. The  $^{19}\text{F}$  NMR datum (Figure 5)  
29 also indicates that the fluorine environment is  
30 contained in a symmetrical field.

31

32 Mass spectroscopic analysis of the product material  
33 confirms the molecular ion mass of the product material  
34 to be 661 amu (Figures 6 and 7). Fragmentation of the  
35 product material is consistent with the loss of the



1 following molecular fragments:-

2		
3	<u>Fragments</u>	<u>Residual Mass (amu)</u>
4		
5	CH <sub>3</sub> - group	647
6		
7	2 @ CH-	632
8		
9	3 @ CH <sub>3</sub> - + 1 @ C <sub>4</sub> H <sub>9</sub> -	558
10		
11	3 @ CH <sub>3</sub> - + 1 @ C <sub>3</sub> H <sub>7</sub> - + 1 @ C <sub>4</sub> H <sub>9</sub> -	516
12		
13	1 @ Au	463
14		
15	1 @ Au + 1 @ C <sub>3</sub> H <sub>7</sub> -	421
16		
17	1 @ Au + 1 @ C <sub>3</sub> H <sub>7</sub> - + 1 @ F	402
18		
19	1 @ Au + 1 @ C <sub>4</sub> H <sub>9</sub> - + 1 @ F	385
20		
21	1 @ Au + 1 @ C <sub>4</sub> H <sub>9</sub> - + 2 @ F	368
22		
23	1 @ Au + 2 @ C <sub>4</sub> H <sub>9</sub> - + 1 @ C <sub>3</sub> H <sub>7</sub> -	
24	+ 2 @ F	269

25

26

27 UV analysis of an evaporated film of organoaurum

28 product supported on quartz shows that the material is

29 uv transparent in the range 900nm-350nm and hence the

30 material is suited for use in mask-making where uv

31 lithography is to be applied.

32

33 Studies have shown that the optimum solvent to be used,

34 both in the abstraction of the product material from

35 the phase separation stage of the preparation and in

1 the deposition of the material onto a quartz substrate,  
2 is a low boiling point saturated alkane. Hence, the  
3 product material was applied to the quartz substrate  
4 using isopentane solvent.

5  
6 The adhesion of organoaurum film to the quartz  
7 substrate material is enhanced by exposing the coated  
8 quartz substrate to microwave radiation prior to  
9 electron beam bombardment. It is thought that this  
10 process effectively evaporates off residual solvent -  
11 trapped between the organoaurum film and the quartz  
12 substrate to give better contact at the interface. The  
13 quartz substrate can also be coated with the  
14 organoaurum material via organometallic vapour  
15 deposition technique (OMVD). The OMVD deposition  
16 method results in a smoother more uniform coverage of  
17 the organoaurum material compared to the solvent  
18 application method.

19  
20 Electron beam bombardment of the coated quartz  
21 substrate was performed using a JEOL JSM-T220 Scanning  
22 Microscope. The microscope was set at an accelerating  
23 voltage of 20kV, focusing and movement of the sample  
24 under the electron beam being both performed manually.  
25 The organoaurum material easily reduced to the metal  
26 component under the electron beam irradiation (Figure  
27 8). The best line width attained to date using the  
28 focussing power available on the JEOL instrument is  
29 500nm.

30  
31 A sample of the dibutylaurum (III) bromide dimer was  
32 applied to the quartz substrate material and subjected  
33 to electron beam bombardment. A film of reduced gold  
34 metal was obtained on the quartz substrate.

35

1 Modifications and improvements can be made without  
2 departing from the scope of the invention, for example  
3 by using vapour phase deposition of the metal-  
4 containing polymer.

5

6

7 Example 3

8

9 Preparation of Dibutylplatinum (IV) Fluoride dimer.

10

11 Magnesium turnings were degreased by washing in sodium  
12 dried ether and transferred to a double-necked round  
13 bottom flask containing a magnetic stirring bar.  
14 Sodium dried ether was added sufficient to cover the  
15 magnesium turnings. The flask was fitted with a water  
16 cooled condenser and a dropping funnel charged with  
17 5.62g dibutyl bromide (Aldrich Chemical Co.) in 80ml of  
18 sodium dried ether. The butylbromide/ ether mixture  
19 was added slowly and allowed to react with stirring  
20 with the magnesium turnings. The system was left to  
21 react for 2 hours at ambient temperature.

22

23 The prepared butylmagnesium bromide/ether mixture was  
24 decanted to a dry dropping vessel and fitted to a  
25 double necked round bottom flask containing 500mg of  
26 platinum (IV) chloride (Aldrich Chemical Co) cooled  
27 with powdered ice. The butylmagnesium bromide mixture  
28 was added slowly with stirring to the platinum (IV)  
29 chloride solution. After reaction powdered ice was  
30 added to the reactant mixture and allowed to warm up to  
31 ambient temperature.

32

33 The dibutylplatinum bromide dimer was extracted from  
34 the reactant mixture using n-pentane in a phase  
35 separation process. A dry methanol/ n-pentane phase

1 separation process was performed a further three times.  
2 The product mixture was reacted with sodium fluoride in  
3 dry methanol as described for the polydibutyltin  
4 difluoride process.

5  
6 The dibutylplatinum (IV) fluoride dimer product was  
7 applied to a clean quartz substrate from an n-pentane  
8 solution and n-pentane was driven off in a microwave  
9 cooker to bake the product onto the quartz. The  
10 microwave process ensured that the n-pentane was driven  
11 off from the quartz interface instead of from its own  
12 surface. This gave very good deposition of the product  
13 on the quartz and allowed very good definition after  
14 electron beam bombardment. A film of reduced platinum  
15 metal was obtained supported on the quartz substrate.

16  
17 A sample of the dibutylplatinum (IV) bromide dimer was  
18 applied to the quartz substrate material and subjected  
19 to electron beam bombardment. A film of reduced  
20 platinum metal was obtained on the quartz substrate.

21  
22 Examples 4-7

23  
24 Preparation of Propyl, Tertiary butyl,  
25 cyclohexylmethyl, benzyl analogues

26  
27 An analogous procedure to that described in Example 2  
28 was performed to prepare the propyl, tertiary butyl,  
29 cyclohexylmethyl and benzyl analogues of organo gold  
30 halides. The preparation of the organo magnesium  
31 halide intermediate involved reaction of degreased  
32 magnesium turnings with the ethereal solutions of the  
33 appropriate propyl, tertiary butyl, cyclohexylmethyl  
34 and benzyl bromides respectively.

35

1     Results:

2

3     a)     NMR analysis of the Propyl Auric Halide Material:

4

5             The  $^1\text{H}$  NMR of the product material from the  
6             reaction of the propyl magnesium Grignard with an  
7             ethereal solution of auric (III) chloride is shown  
8             in figure 9. The NMR shows peaks at 0.89 ppm  
9             (triplet), and 1.29 ppm (multiplet) relative to  
10            TMS (tetramethylsilane), which is consistent with  
11            the spectrum expected from the propyl ligand. The  
12            broad band at 1.57 ppm is consistent with that  
13            expected for the  $-\text{CH}_2-$  adjacent to a group inducing  
14            electron shielding. The  $^{13}\text{C}$  NMR is shown in Figure  
15            10. Although noisy, the spectrum shows three  
16            peaks at 14 ppm, 22 ppm and 33 ppm relative to  
17            TMS. The  $^{13}\text{C}$  environments are consistent with  $\text{CH}_3$ ,  
18             $-\text{CH}_2-$  and a shielded  $-\text{CH}_2-$  respectively. The  $^{19}\text{F}$   
19            NMR of the sample (proton coupled and decoupled)  
20            showed a singlet at -67.64 ppm relative to  $\text{CCl}_3\text{F}$   
21            indicating that the material contained fluorine in  
22            a symmetrical field.

23

24            The product material was applied to a quartz  
25            substrate as described in Example 2. Electron  
26            beam bombardment was applied to the coated quartz  
27            material as described in Example 2. The material  
28            reduced under the electron beam bombardment to  
29            give gold lines identical to those obtained from  
30            the tetrabutyl diaurum difluoride material.

31

32     b)     NMR analysis of the Benzyl Auric Halide Material:

33

34            The  $^1\text{H}$  NMR spectrum of the product material is  
35            presented in figure 11. The NMR data shows major

1 peaks at 7.3 ppm (multiplet) and 2.9 ppm (singlet)  
2 relative to TMS. Smaller peaks consistent with  
3 trace quantities of isopentane are also evident.  
4 The spectrum shows that the product material  
5 contains ligated benzyl groups. The  $^{13}\text{C}$  spectrum  
6 is presented in figure 12. The spectrum shows  
7 peaks at 141.7 ppm, 128.5 ppm, 128.3 ppm, 125.9  
8 ppm and 37.9 ppm relative to TMS. The  $^{13}\text{C}$   
9 environments are consistent with the distribution  
10 of shielding effect over the benzyl group ligated  
11 to an electron inducing species. The  $^{19}\text{F}$  NMR  
12 showed a singlet at -67 ppm relative to CFC-11,  
13 similar to those obtained for the previous  
14 samples.

15  
16 The product material from the benzyl Grinard  
17 reagent reaction with an ethereal solution of auric  
18 (III) chloride was applied to a clean quartz  
19 substrate and subjected to electron beam  
20 bombardment as described in Example 2. The  
21 material did not reduce to give metal lines.

22  
23 c) NMR analysis of the t-Butyl Auric Halide material.

24  
25 The  $^1\text{H}$  NMR analysis of the product material from  
26 the reaction of the t-butyl Grinard reagent with  
27 an ethereal solution of auric (III) halide is  
28 presented in figure 13. The NMR data shows the  
29 presence of a major peak at 1.24 ppm (singlet)  
30 relative to TMS which is consistent with that  
31 expected for the t-butyl group. Impurities in the  
32 NMR have been identified to be MeOH, TMS and  $\text{CHCl}_3$ .  
33 Peaks consistent with some trace hydrocarbon  
34 solvent are also observed. The  $^{19}\text{F}$  NMR analysis  
35 showed one peak at -67 ppm relative to CFC-11.

1 The product material from the reaction was applied  
2 to a clean quartz substrate and subjected to  
3 electron beam bombardment as described in Example  
4 2. The material did not reduce to give gold metal  
5 lines.

6  
7 d) NMR analysis of the Cyclohexylmethyl Auric (III)  
8 Material:

9  
10 The  $^{13}\text{C}$  NMR spectrum is presented in figure 14.  
11 The spectrum shows peaks at 36.15 ppm, 34.67 ppm,  
12 33.6 ppm and a doublet at 26.6 ppm relative to  
13 TMS. The spectrum is consistent with that  
14 expected for methyl cyclohexane. The  $^1\text{H}$  NMR  
15 analysis is presented in figure 15. The spectrum  
16 shows peaks at 1.2 ppm, (singlet) 1.6 and 1.7 ppm  
17 (singlets), 2.9 and 3.25 ppm (doublets). The  
18 spectrum is consistent with that of  
19 methylcyclohexane. The  $^{19}\text{F}$  spectrum is shown in  
20 figure 16. A singlet peak at -68 ppm relative to  
21 CFC-11 is again observed.

22  
23 The product material from the methylcyclohexyl  
24 aurum reaction was applied to a clean quartz  
25 substrate and subjected to electron beam  
26 bombardment as described in Example 2. The  
27 material did reduce under the conditions used to  
28 deposit fine lines of gold as observed under  
29 optical magnification. The width of the gold  
30 lines obtained were ca 500nm.

31  
32  
33 Example 8

34  
35 Preparation of organoplatinum halide complex:

1 The preparation of platinum analogue materials was  
2 performed analogously to those described in Example 2.  
3 Propyl, butyl and methylcyclohexane analogues were  
4 prepared. The respective organomagnesium halide  
5 intermediate material was reacted with an ethereal  
6 solution of platinum (IV) chloride (Johnson Matthey) at  
7 0°C. Phase separation of the product material was  
8 performed as described in Example 2. The product  
9 material obtained had a white waxy appearance similar  
10 to that obtained from the gold complexes.

### 11 12 13 Results

#### 14 15 a) NMR analysis of the product material from t-Butyl 16 platinum fluoride:

17  
18 The <sup>1</sup>H NMR analysis is presented in figure 17. The  
19 NMR shows the major peak at 1.25 ppm (singlet)  
20 with evidence of MeOH solvent in the sample. The  
21 <sup>19</sup>F NMR analysis gave one peak at -67.66 ppm.

#### 22 23 b) NMR analysis of the Butyl platonic halide product.

24  
25 The <sup>1</sup>H NMR of the product obtained from the  
26 reaction of the n-butyl Grignard reagent with an  
27 ethereal solution of platinum (II) chloride is  
28 presented in figure 18. The NMR shows peaks at  
29 0.82 ppm (doublet), 1.28 ppm (singlet), 1.39 ppm  
30 (singlet) and 1.5 ppm (singlet), relative to TMS.  
31 The spectrum is consistent with that expected for  
32 an n-butyl moiety. The <sup>19</sup>F NMR analysis of the  
33 material showed a singlet peak at -67 ppm (Figure  
34 19).

35



1 The product material was applied to a clean quartz  
2 substrate and subjected to electron beam  
3 bombardment as described in Example 2. The  
4 material was readily reduced under the influence  
5 of the electron beam to deposit a line of metallic  
6 appearance.

7

8 c) NMR Analysis of the Propyl Platinic Fluoride  
9 Material:

10

11 The  $^1\text{H}$  NMR spectrum was performed in deuterobenzene  
12 solvent and is presented in figure 20. The  
13 spectrum shows peaks at 1.33 ppm (singlet),  
14 0.91ppm (singlet) and 0.39 ppm (singlet) relative  
15 to TMS. The spectrum is consistent with that  
16 expected for a propyl moiety.  $^{19}\text{F}$  NMR analysis  
17 gave a single peak at -67 ppm.

18

19 d) NMR Analysis of the Methylcyclohexyl Platinic  
20 Fluoride Material:

21

22 The  $^1\text{H}$  NMR spectrum of the product material from  
23 the reaction of the methylcyclohexyl Grignard  
24 reagent with an ethereal solution of platinum (II)  
25 chloride is presented in figure 21. The spectrum  
26 is consistent with that expected for the  
27 methylcyclohexyl ligand. The  $^{13}\text{C}$  carbon NMR is  
28 also presented in figure 22. The spectrum also  
29 confirms that the product material contains  
30 ligated methylcyclohexyl groups.

31

32

33 Example 9

34

35 Example of the Butylpalladium analogue complex:

1 The preparation of the butyl palladium analogue was  
2 performed as described in Example 2. The respective  
3 organomagnesium halide intermediate material was  
4 reacted with an ethereal solution of palladium (II)  
5 chloride. It was observed that the product material  
6 was thermally unstable resulting in deposition of the  
7 palladium component at around 50°C. The deposited  
8 palladium metal had strongly adhered to the glass  
9 surface and could only be removed using acids.

10

# 11 Results

12

13 The <sup>1</sup>H NMR analysis of the product material from the  
14 butyl Grignard reagent with an ethereal solution of  
15 palladium (II) chloride is presented in figure 23. The  
16 spectrum is consistent with that expected for a butyl  
17 ligand a weak interaction with the ligated centre. The  
18 <sup>13</sup>C NMR spectra shows the presence of 3 carbon  
19 environments in the compound. The <sup>19</sup>F NMR again shows a  
20 singlet peak at -67 ppm (Figure 25)..

21

22

# 23 General Discussion

24

25 Examples 2 to 9 show that the butyl-, propyl- and  
26 cyclohexyl- gold complexes are able to be reduced to  
27 the metal component under electron beam bombardment.  
28 The preparation of the propyl- and cyclohexyl-  
29 analogues of the gold complex show no rearrangement  
30 during the synthesis treatment. The <sup>1</sup>H NMR spectra of  
31 these compounds do not exhibit any splitting patterns  
32 that are consistent with the incorporation of fluorine  
33 into the organic ligand. Whether these compounds have  
34 fluorine as a constituent in their structure remains to  
35 be determined. The <sup>19</sup>F NMR signal for the product

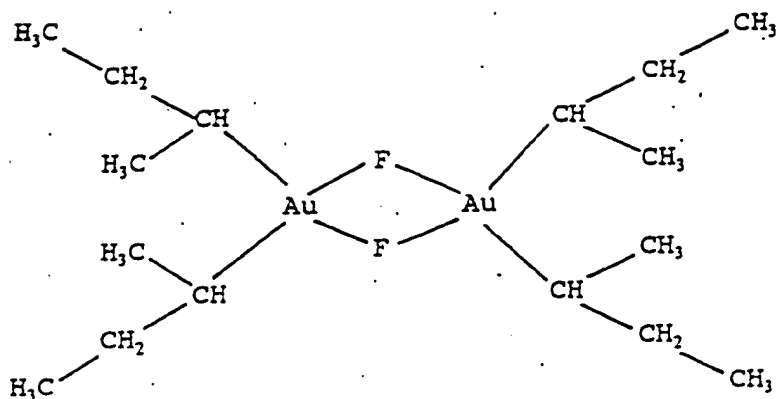
1 materials indicate that fluorine is present in a form  
2 which confers a symmetrical field around the fluorine  
3 environment. Given that fluorine has the ability to  
4 affect neighbouring carbon atoms and cause coupling  
5 over long ranges, it seems that whatever form the  
6 fluorine is in, it is shielded from the organic ligands  
7 so that coupling cannot take place.

8

9 The reaction of the n-butyl group to give sec-butyl  
10 products gives rise to some questions about the  
11 chemistry that is affecting the formation of the  
12 butylauric (III) fluoride. Firstly, it is important to  
13 note that the organic ligand itself does not contain  
14 fluorine. No splitting of the proton signals are  
15 observed in the proton spectra and there are no signals  
16 in the  $^{19}\text{F}$  NMR to indicate that hydrofluoroalkane groups  
17 are present. Hence, the isomerisation step of the n-  
18 alkane cannot be taking place during the fluorination  
19 process. Isomerisation usually requires the production  
20 of a carbocation species in the presence of  $\text{F}^-$  ions  
21 during the reaction with the methanol solution of  $\text{NaF}$   
22 would immediately give rise to a fluorinated organic  
23 ligand, for which there is no evidence. Hence, the  
24 evidence suggests an intramolecular re-arrangement at  
25 some stage in the production of the fluorided material.

26

27 The mass spectroscopic data gives a molecular ion of  
28 661 amu, the fragmentation pattern of which is wholly  
29 consistent with the formula  $(\text{sec-butyl})_4\text{Au}_2\text{F}_2$ . It must  
30 be remembered that the Au (III) is in a  $5d^8$   
31 configuration that would give a square planar  
32 arrangement, and would also consider the propensity of  
33 gold to form bridging dimers. Thus, it is tentatively  
34 submitted that the tetrakis sec-butyl aurum (III)  
35 difluoride structure would be as follows:



The organoaurum product is uv transparent in the region from 900-3500nm. This is a positive result should mask-making be an application for the material.

No deposition of metal lines was obtained from the benzyl- and tertiary butyl- analogues. These materials possess good inductive properties and are able to pump electron density into neighbouring moieties. This may have an effect on the reducibility of the gold complexes.

Electron reduction has been successfully shown on the butyl analogue of the Pt material. Also the cyclohexyl analogue of the Pd materials were able to be reduced by electron beam bombardment techniques. Thermal degradation of the palladium complex at 50°C resulted in a strongly bound metallic film of palladium that could only be removed by reaction with acid. This result indicates that the palladium analogue of the organometallic complexes is a suitable candidate for metal deposition by laser degradation.

1     CLAIMS

2

3

4     1.    A method of chemical deposition comprising  
5           applying to a substrate a compound which degrades  
6           under the effect of a radiant or particle beam to  
7           produce a deposit and a degraded compound residue,  
8           applying to selected areas of said compound a  
9           radiant or particle beam and removing the degraded  
10          compound residue and unaffected compound from said  
11          substrate.

12

13    2.    A method as claimed in Claim 1 for manufacturing  
14          an integrated circuit wherein said deposit is a  
15          conductive material.

16

17    3.    A method as claimed in Claim 1 for manufacturing a  
18          photomask wherein said substrate is a transparent  
19          or translucent material and wherein said deposit  
20          is opaque.

21

22    4.    A method as claimed in any one of Claims 1 to 3  
23          wherein said compound is an organometallic  
24          material.

25

26    5.    A method as claimed in any one of Claims 1 to 4  
27          wherein said compound is an organometallic  
28          fluoride.

29

30    6.    A method as claimed in any one of Claims 1 to 5  
31          wherein said compound is an organometallic gold,  
32          platinum, palladium or tin fluoride.

33

34    7.    A method as claimed in any one of Claims 1 to 6  
35          wherein said compound is tetra-sec butyl diaurum

1 difluoride.

2

3 8. A method as claimed in any one of Claims 1 to 7  
4 wherein said compound is exposed to microwave  
5 radiation after application to said substrate and  
6 before application of said radiant or particle  
7 beam.

8

9 9. A method as claimed in any one of Claims 1 to 7  
10 wherein said compound is applied to said substrate  
11 by an organometallic vapour deposition (OMVD)  
12 technique.

13

14 10. A method as claimed in any one of Claims 1 to 9  
15 wherein said compound is degraded by a laser beam,  
16 an ultra-violet beam and/or an electron beam.

17

18 11. An integrated circuit obtainable by the method as  
19 claimed in any one of Claims 1, 2 and 4 to 10.

20

21 12. A photomask obtainable by the method as claimed in  
22 any one of Claims 1 and 3 to 10.

23

24 13. An integrated circuit or photomask as claimed in  
25 either of Claims 11 and 12 having nanoscale  
26 resolution.

27

28 14. An integrated circuit manufactured by use of a  
29 photomask as claimed in either of Claims 12 and  
30 13.

31

32 15. A gold organometallic fluoride compound..

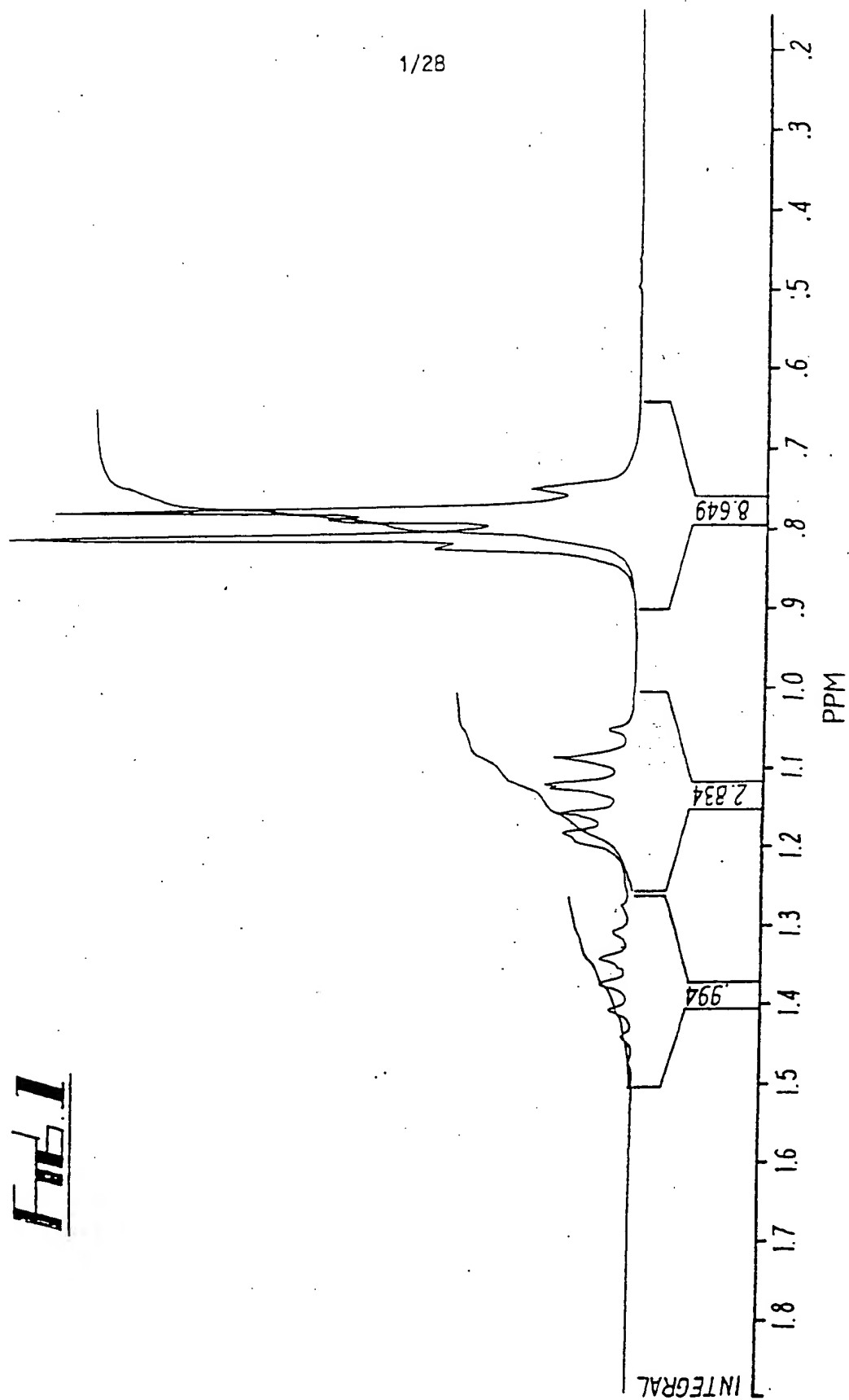
33

34 16. Use of an organometallic compound in a method as  
35 claimed in any one of Claims 1 to 10.

- 1     17. Use as claimed in Claim 16 wherein said  
2         organometallic compound is an organometallic gold,  
3         platinum, palladium or tin fluoride compound.  
4
- 5     18. Use of a radiant or particle beam in the method as  
6         claimed in any one of Claims 1 to 10.  
7
- 8     19. A method of manufacturing an organometallic  
9         fluoride compound suitable for use in the method  
10        of Claims 5 to 10, wherein sodium fluoride is  
11        added to said organometallic compound in its  
12        chloride or bromide form.  
13  
14

1/28

Fig. 1





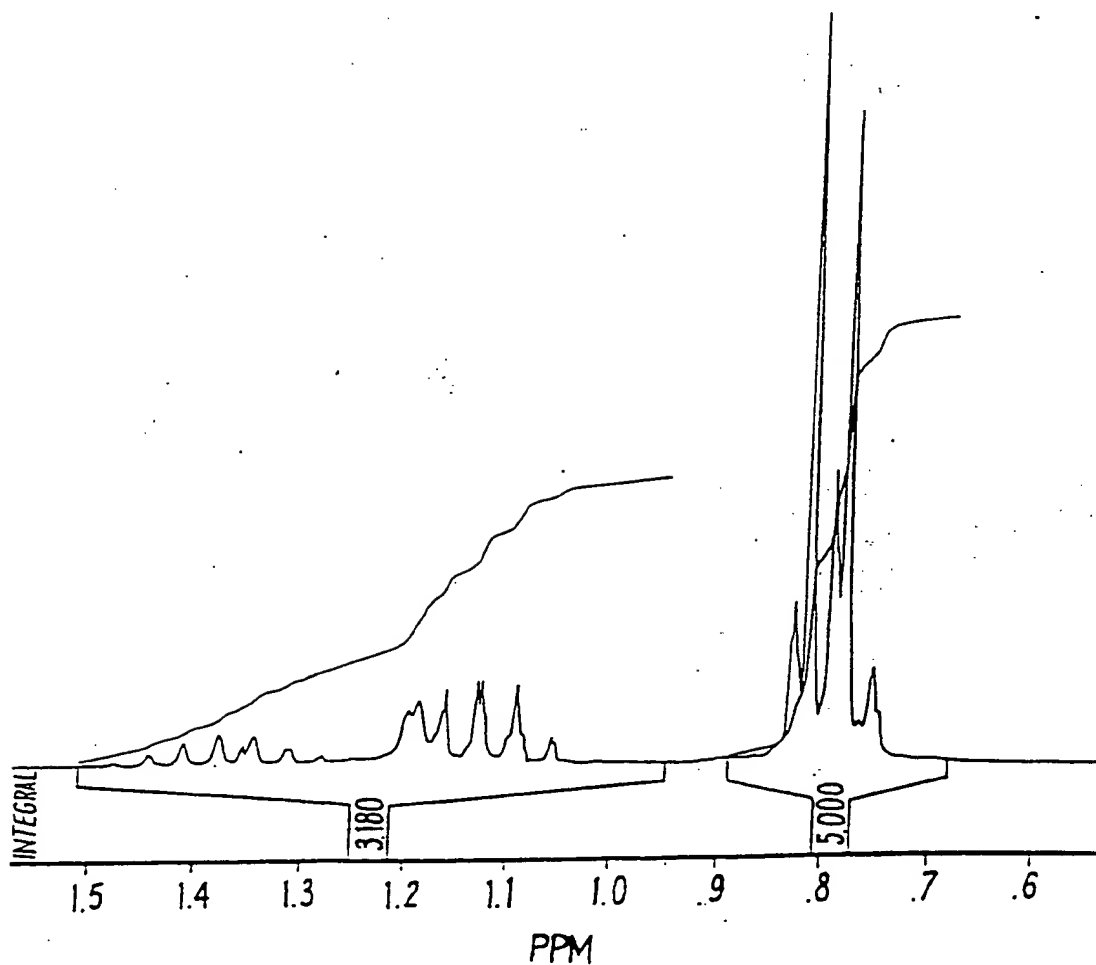


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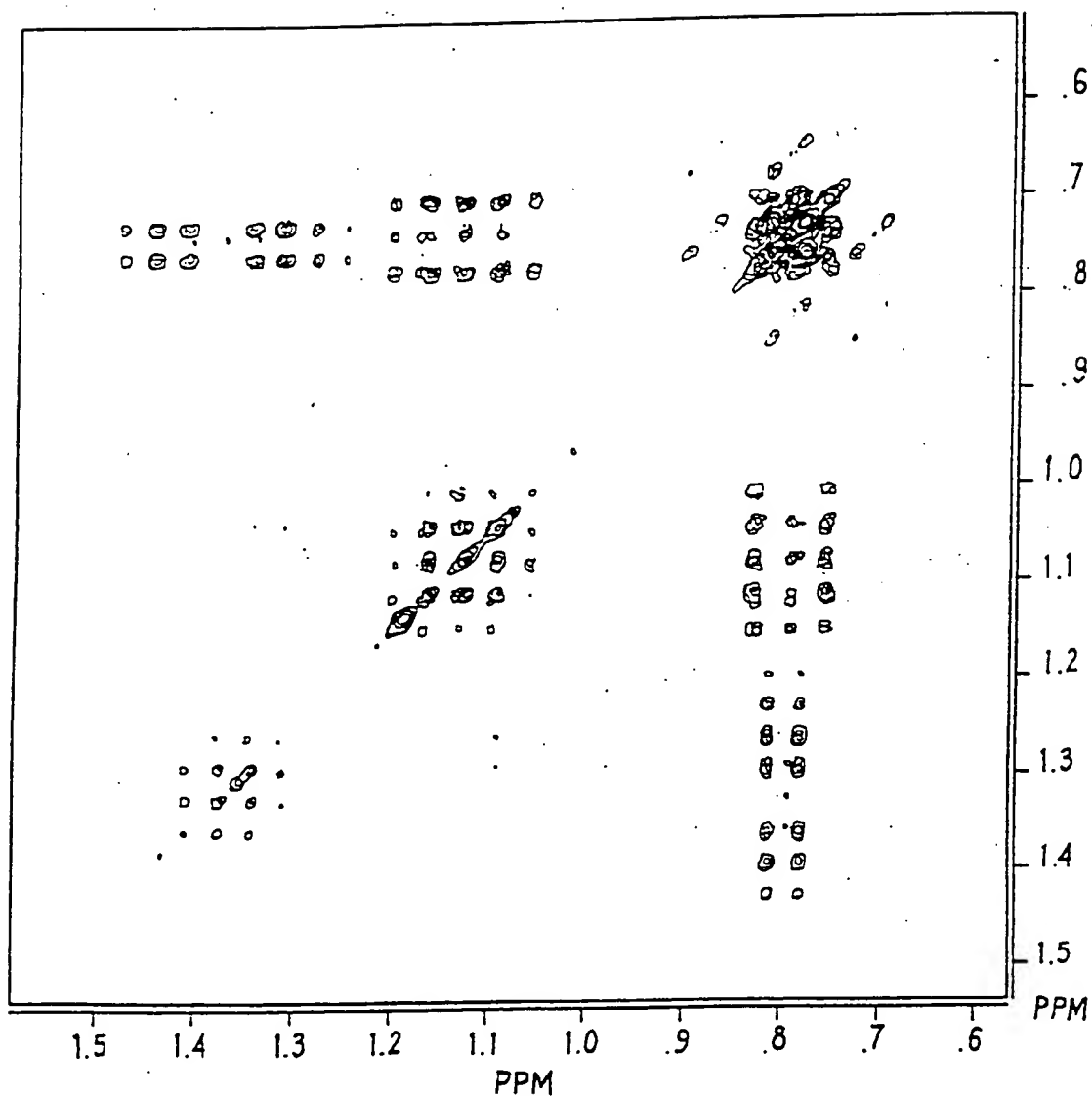
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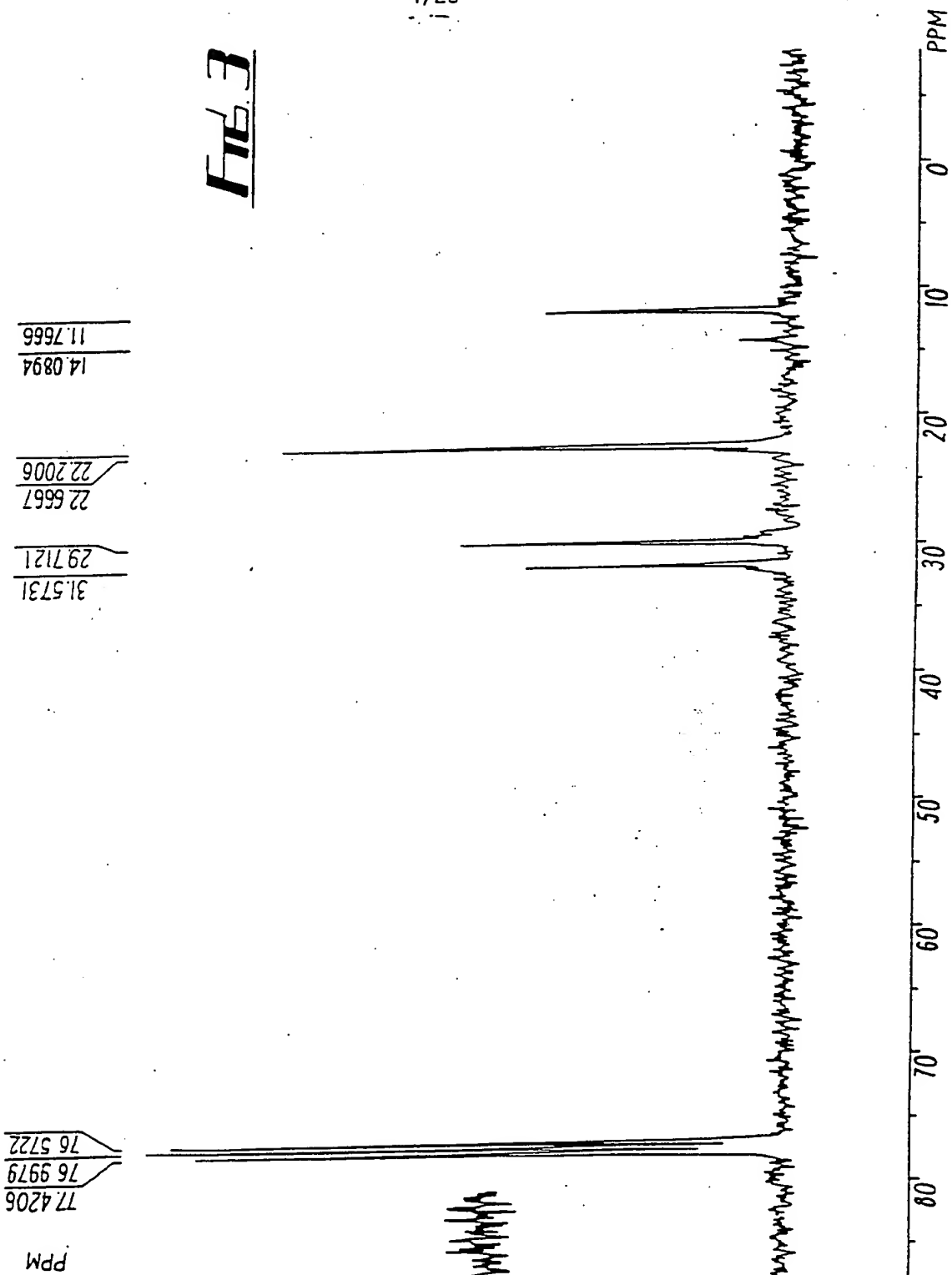
**Fig. 1a**

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FIG. 2

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**Fig. 3**



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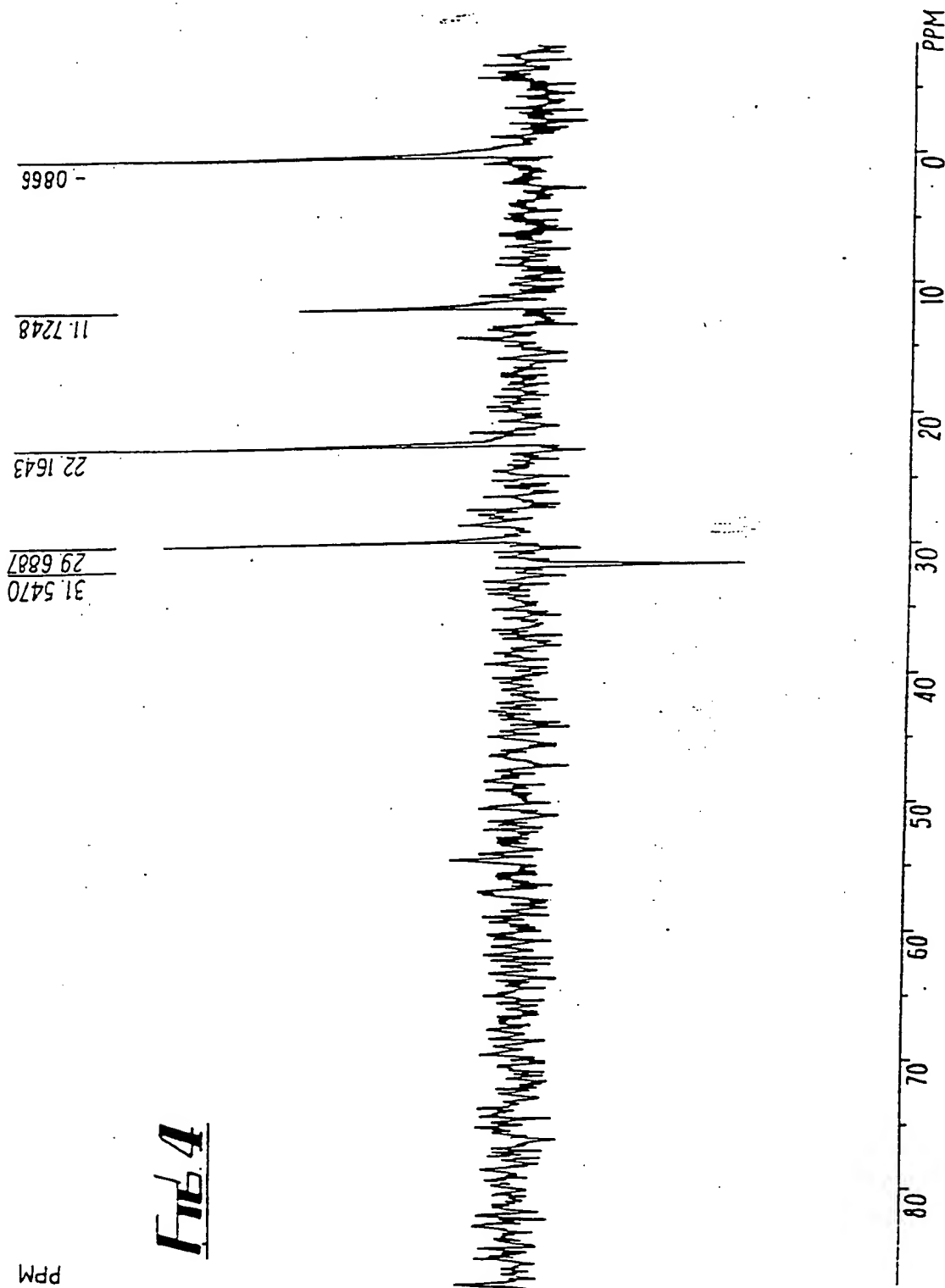


Fig 4

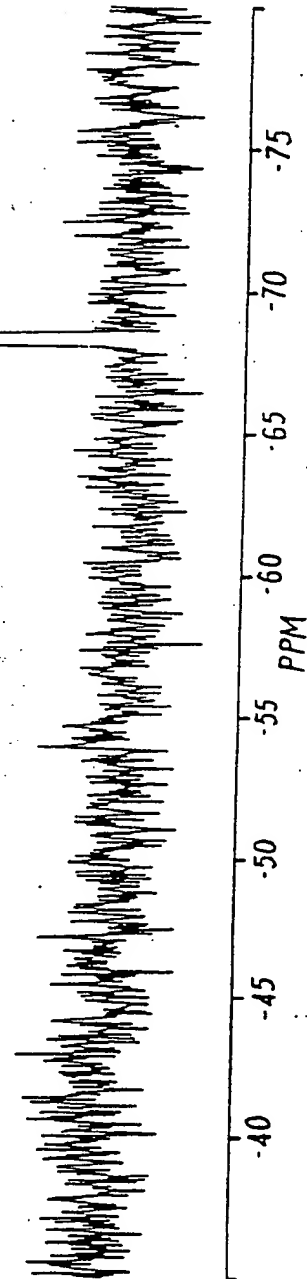
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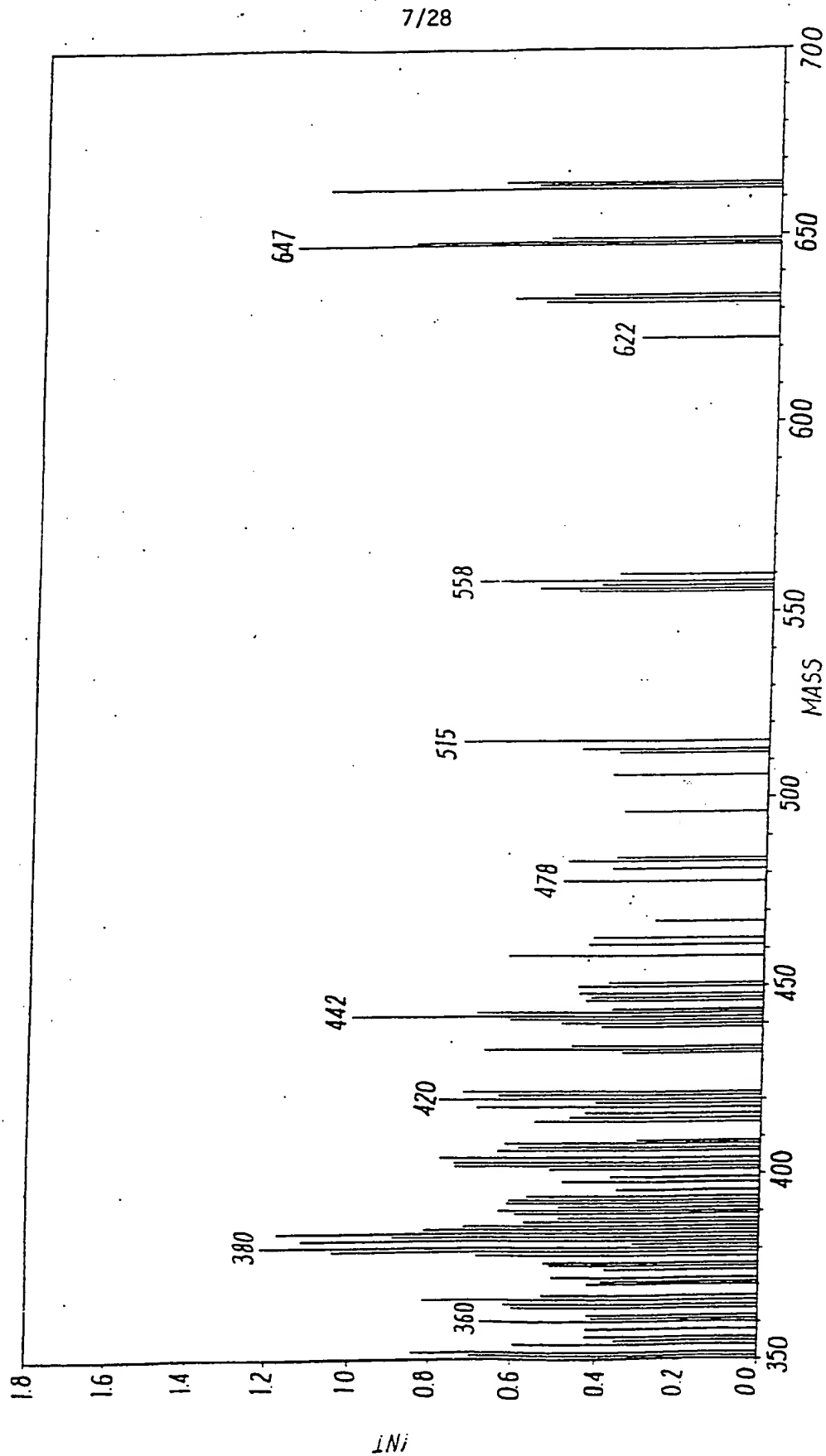
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Fig. 5

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PPM



**FILE 6**

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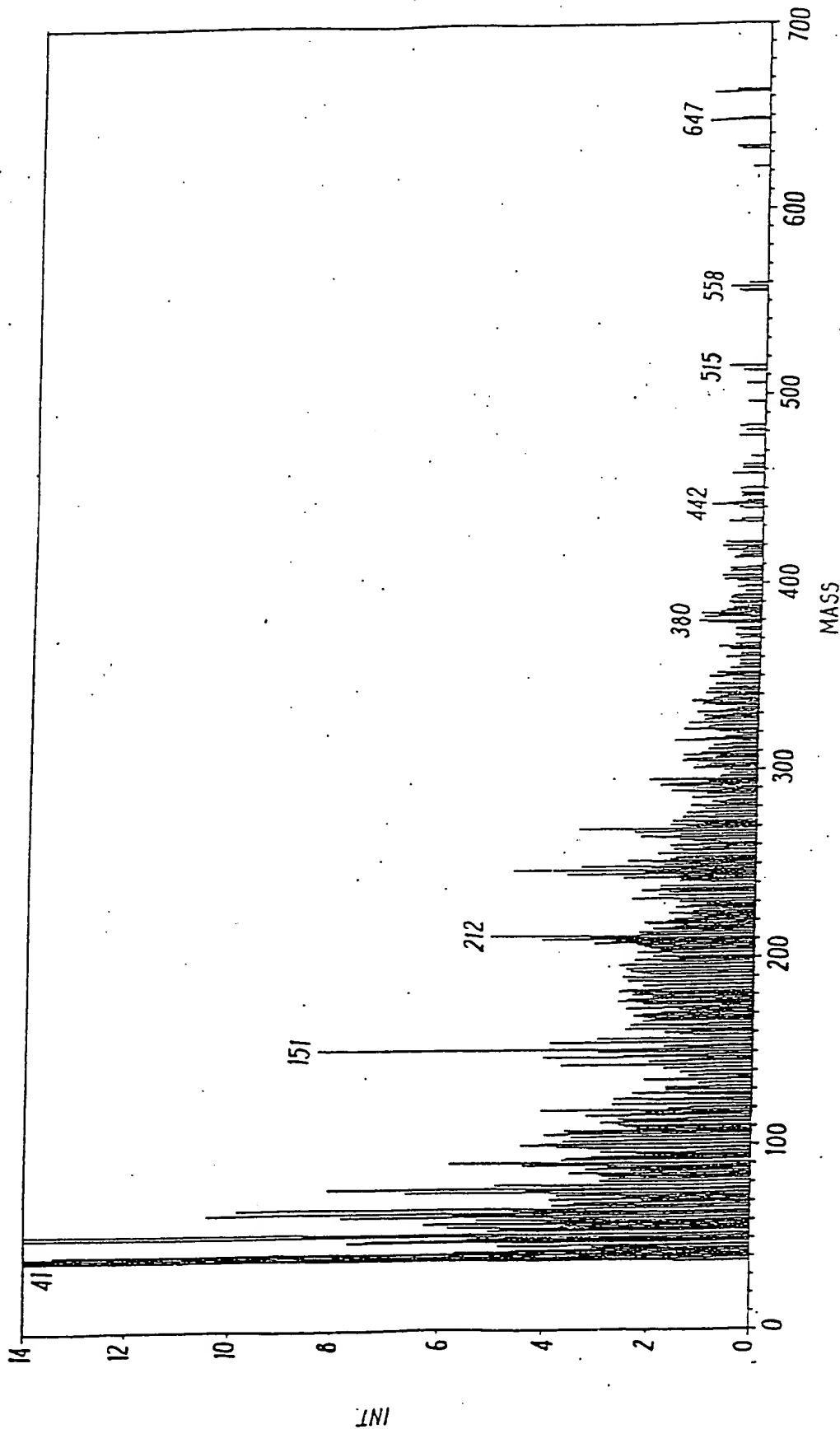
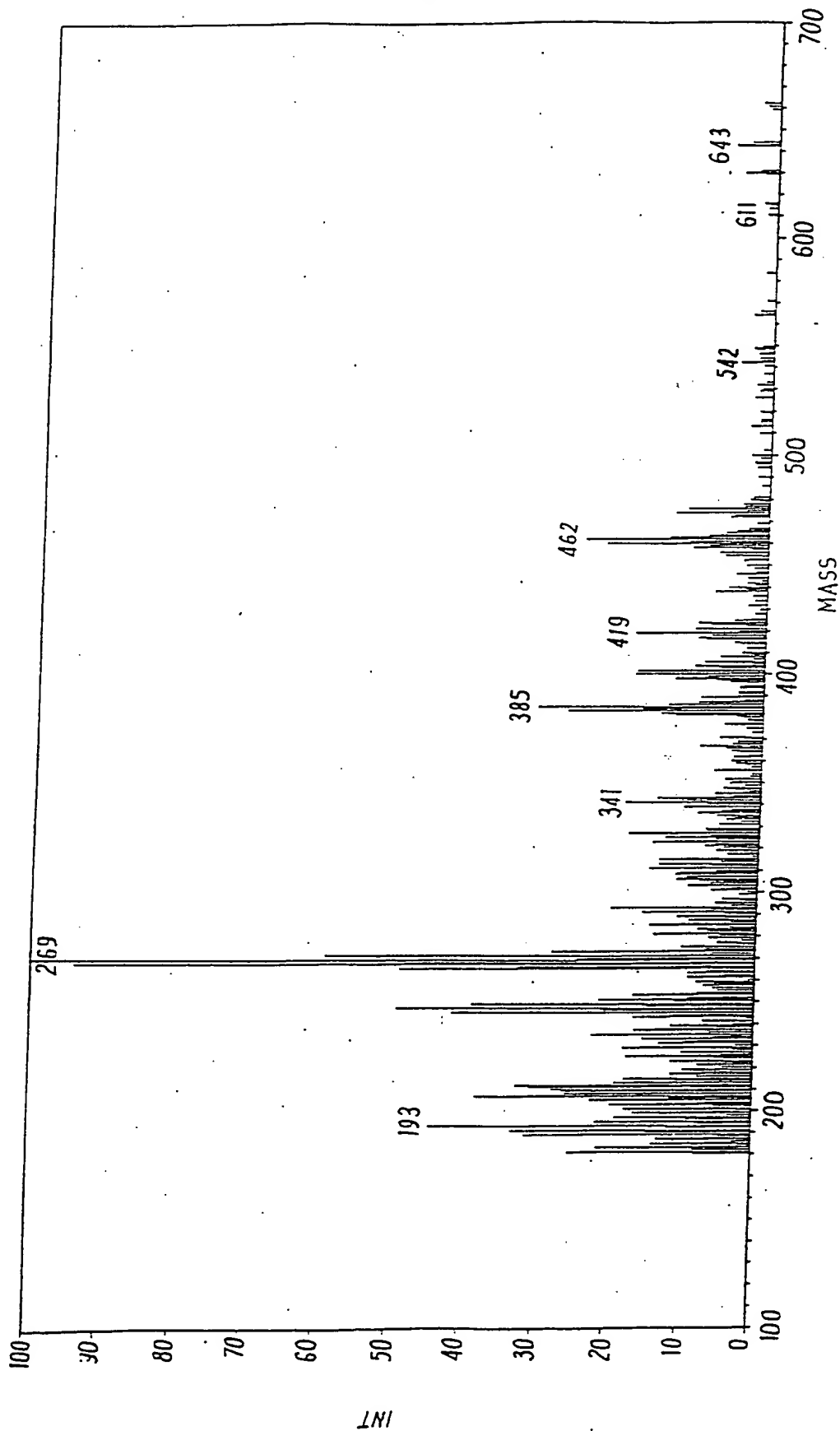


Fig. 6a



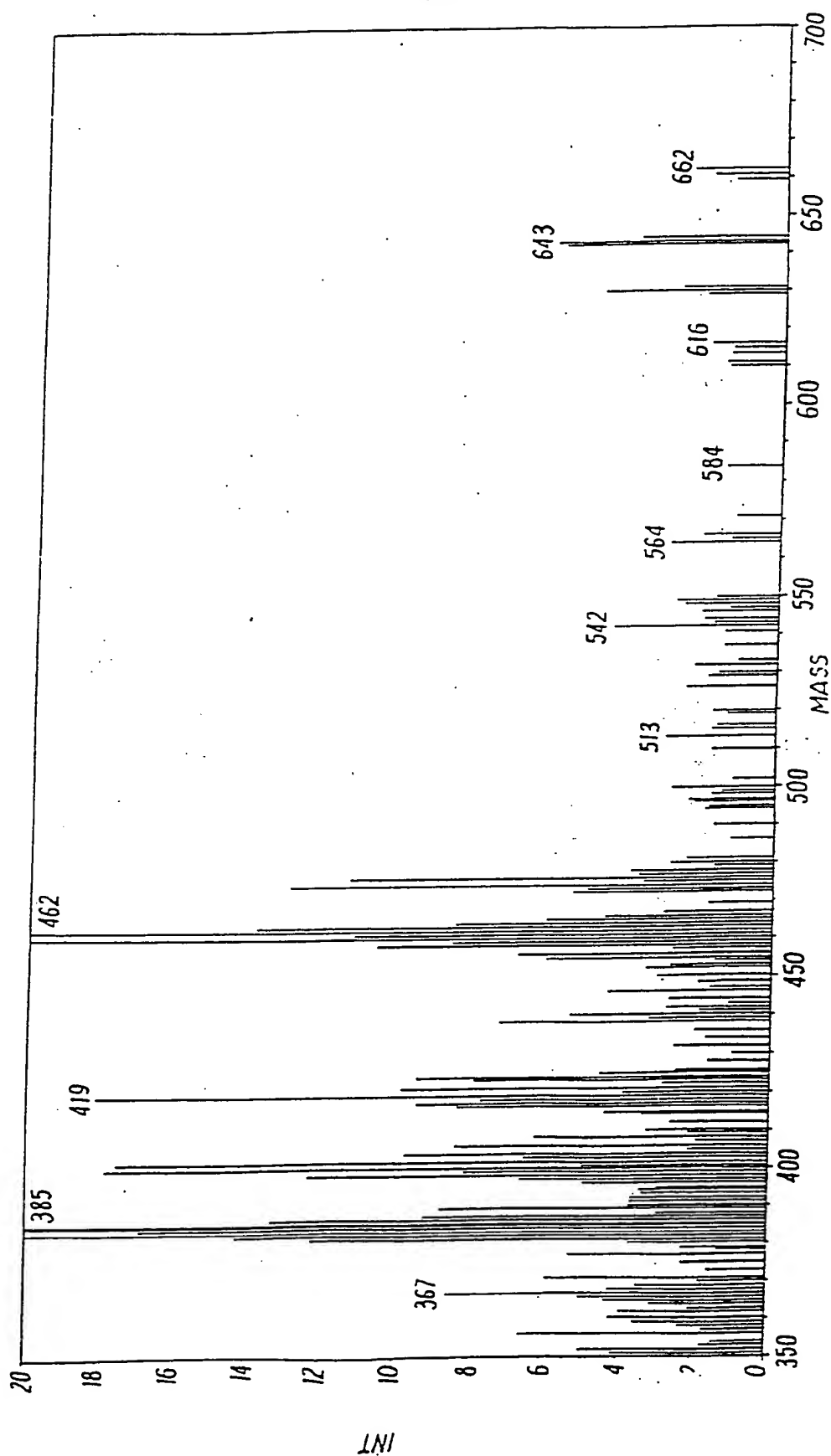
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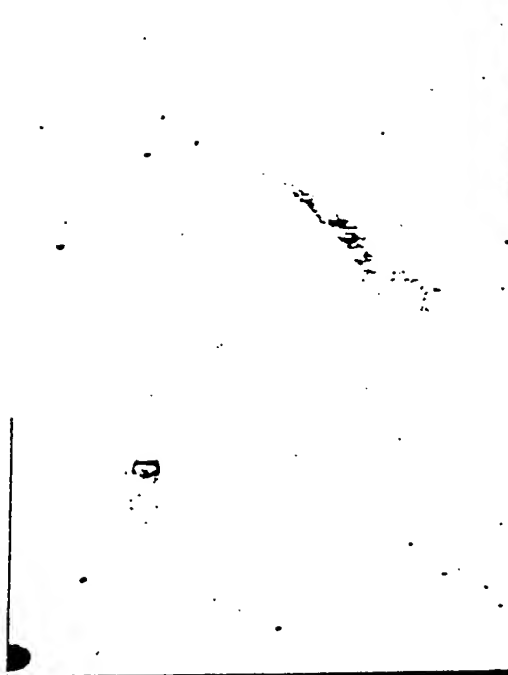
MASS

**Fig. 7**

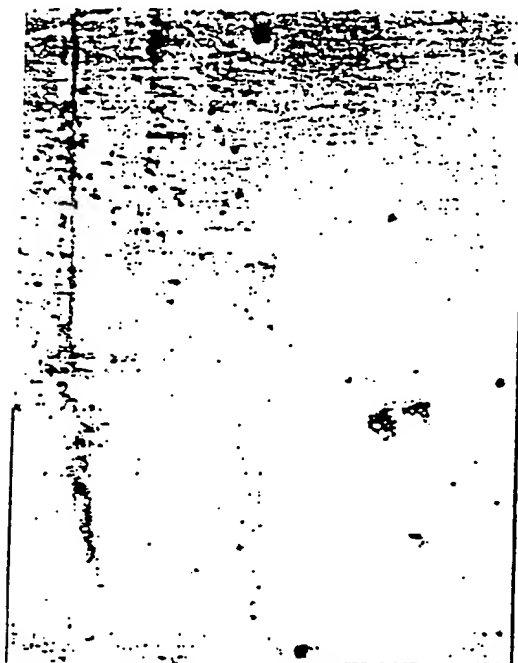
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Fig. 1a

11/28



**Fig. 8**



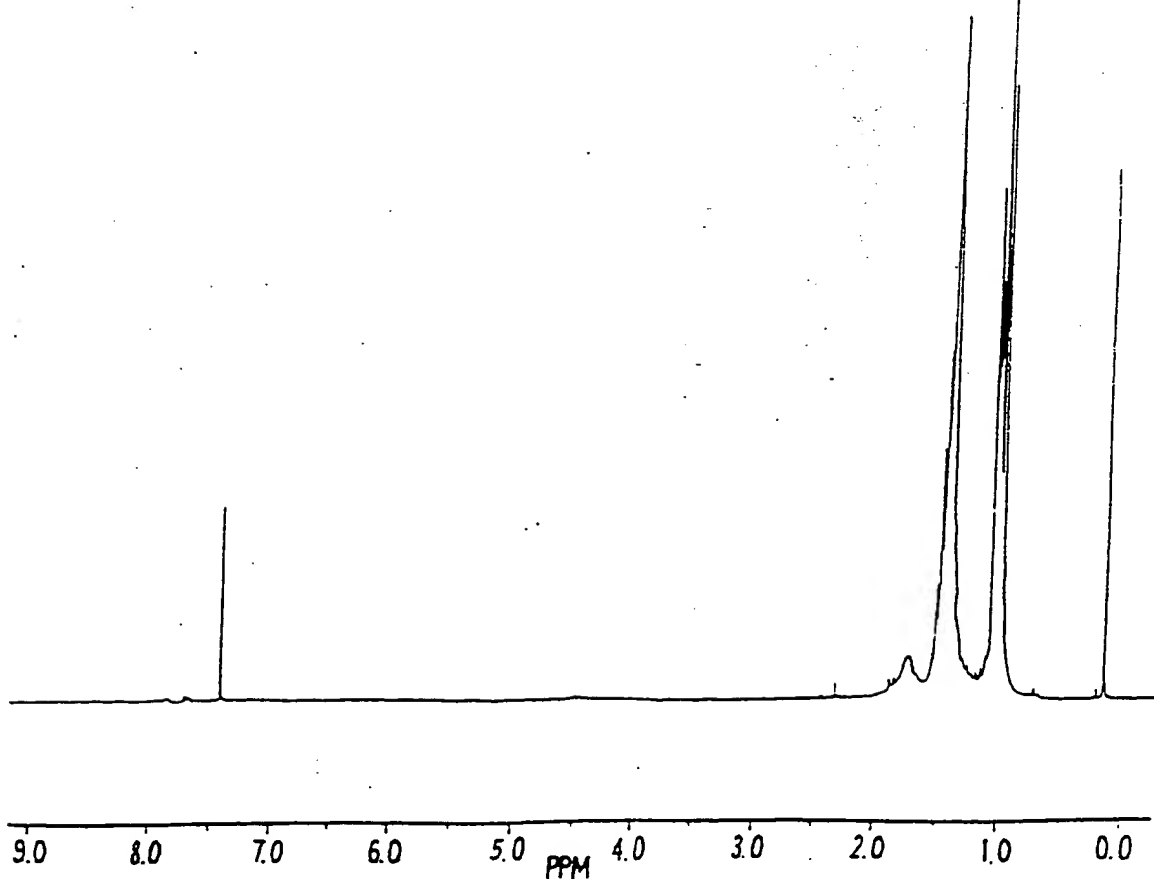
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PPM

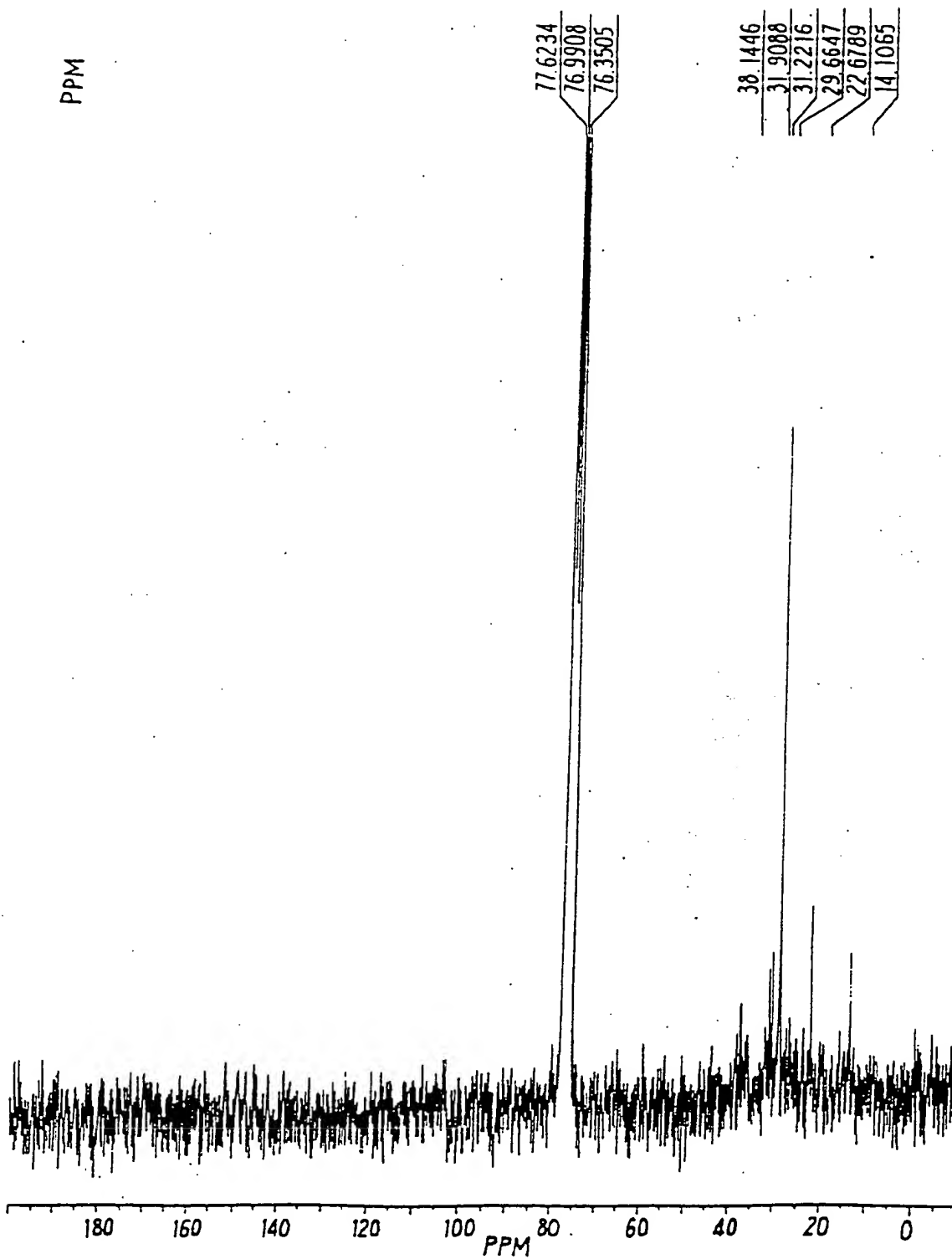
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89766  
88288  
84751  
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File 9



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FIG. 10

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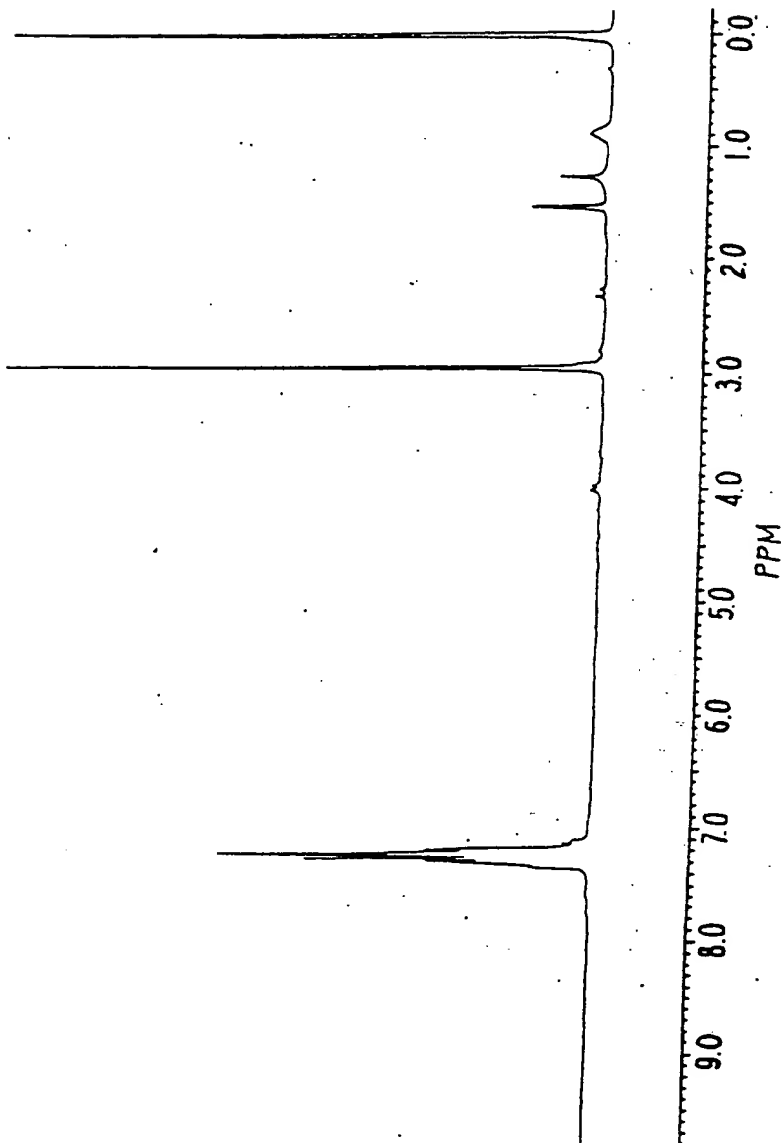
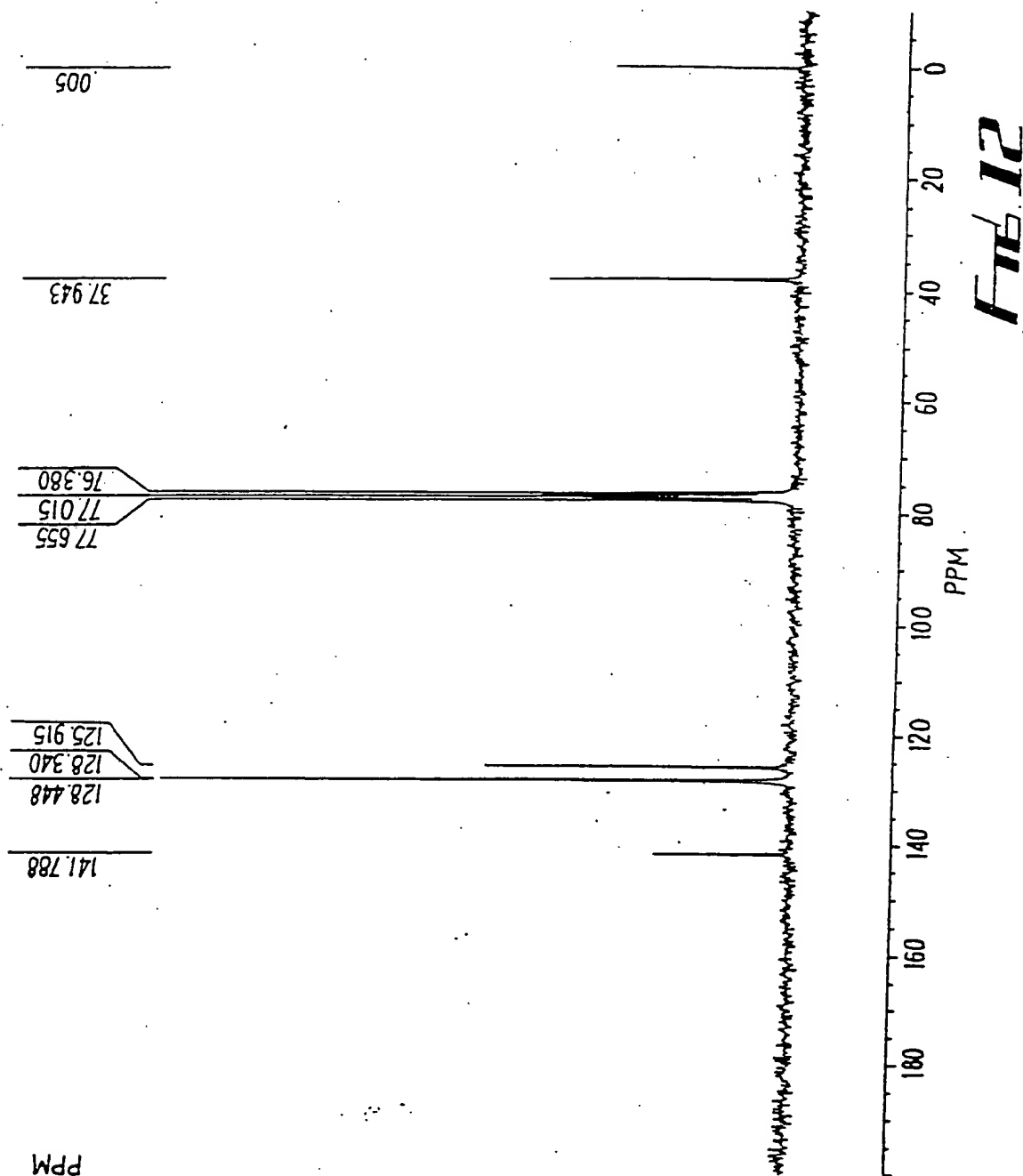
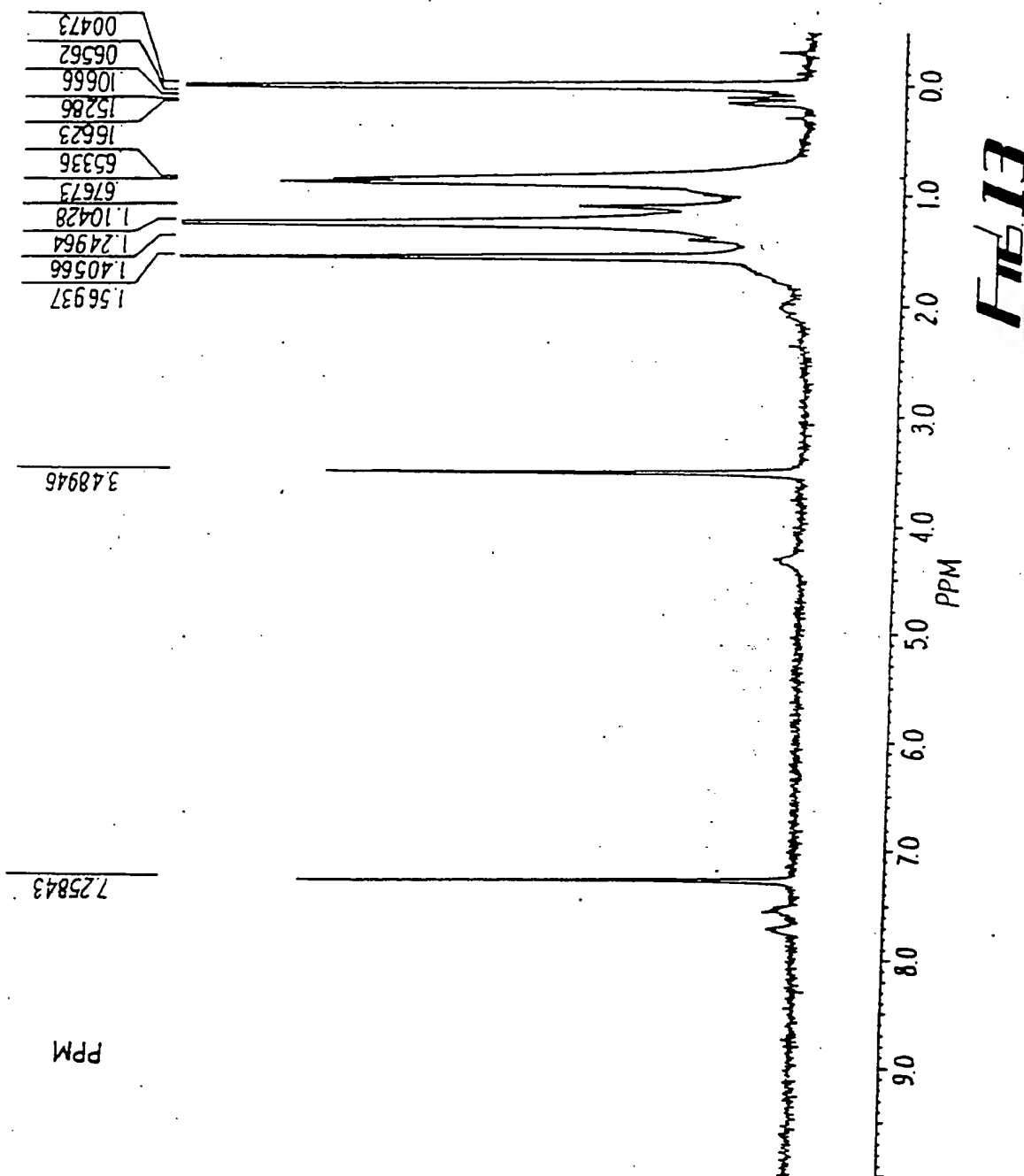


Fig. 11

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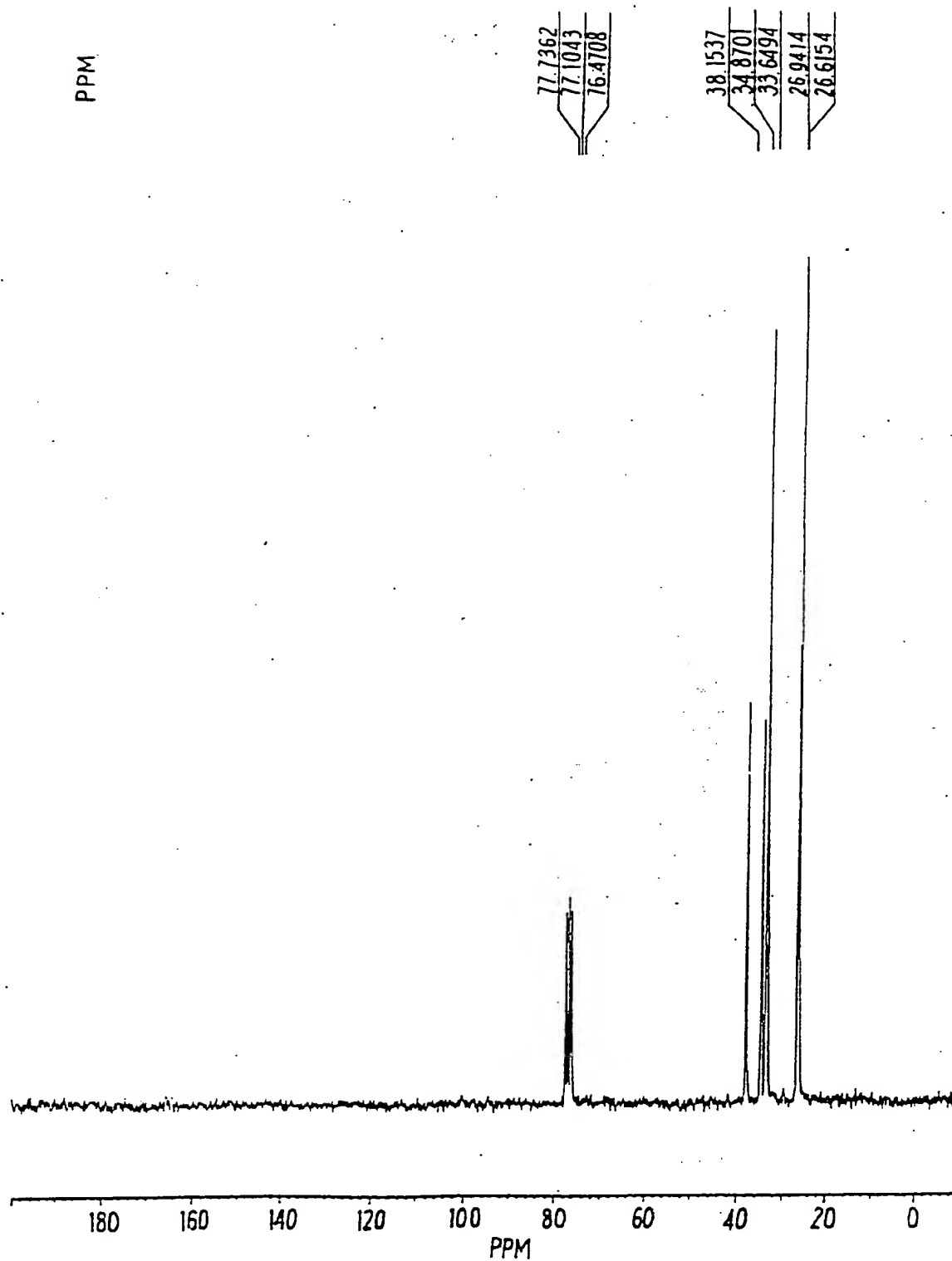


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FIG. 14

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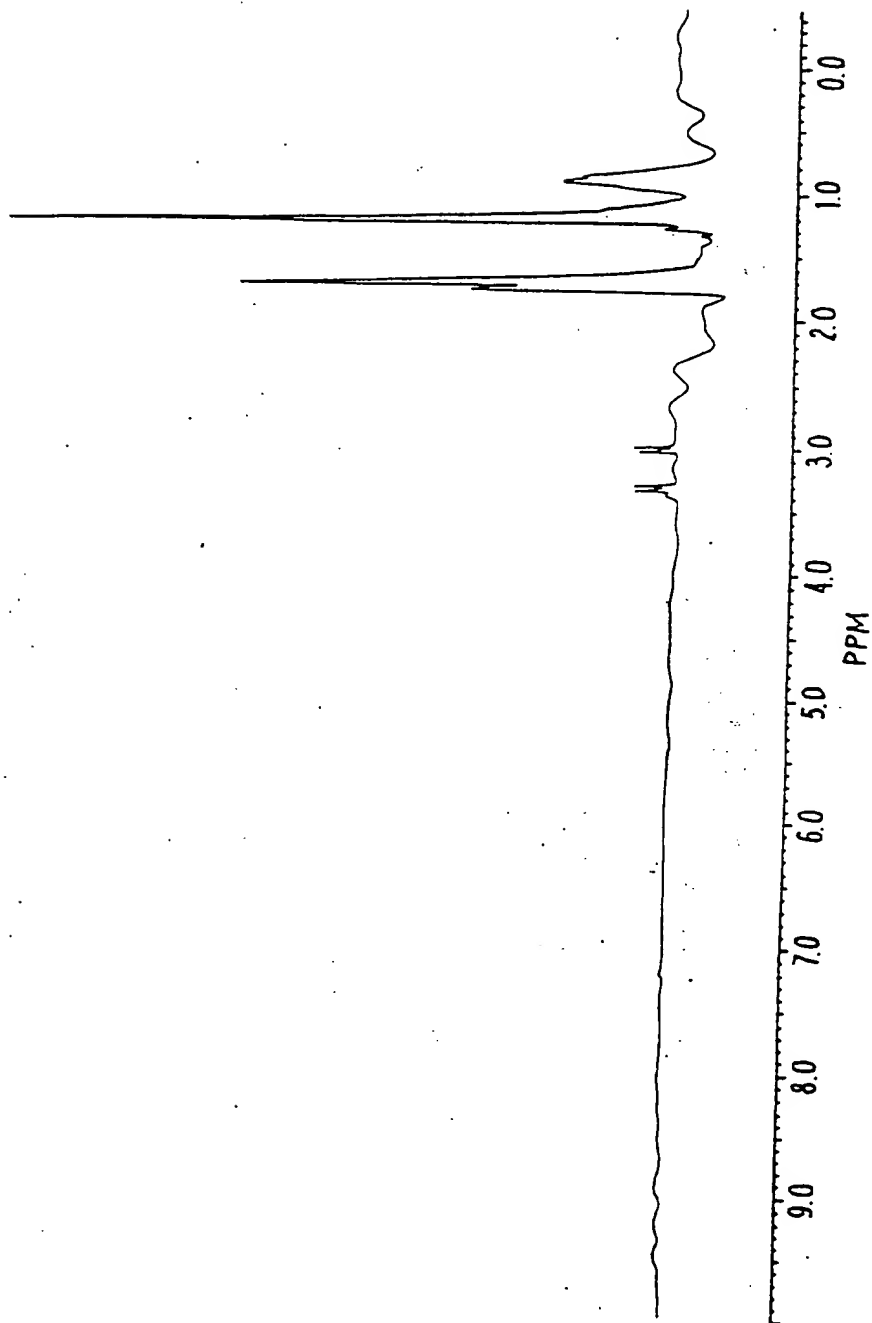


FIG 15

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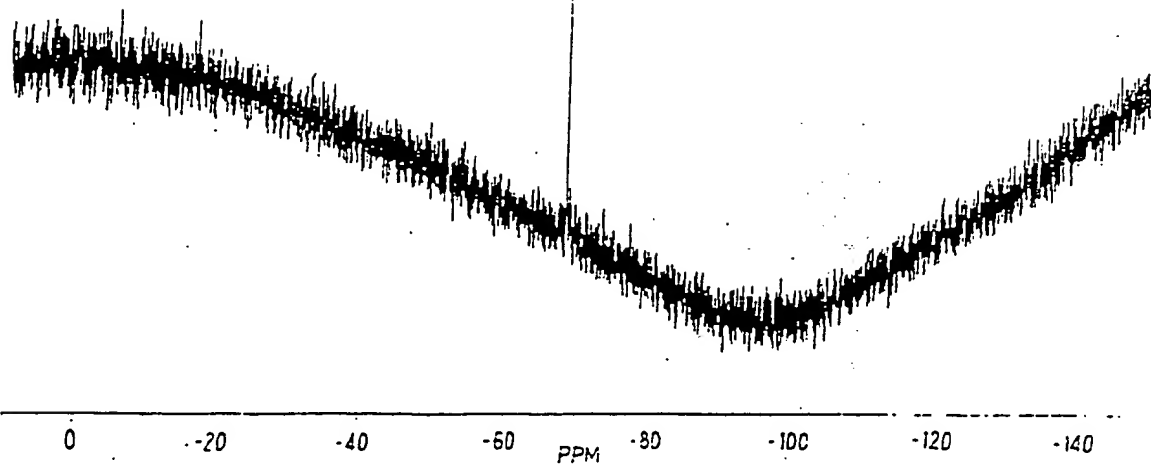
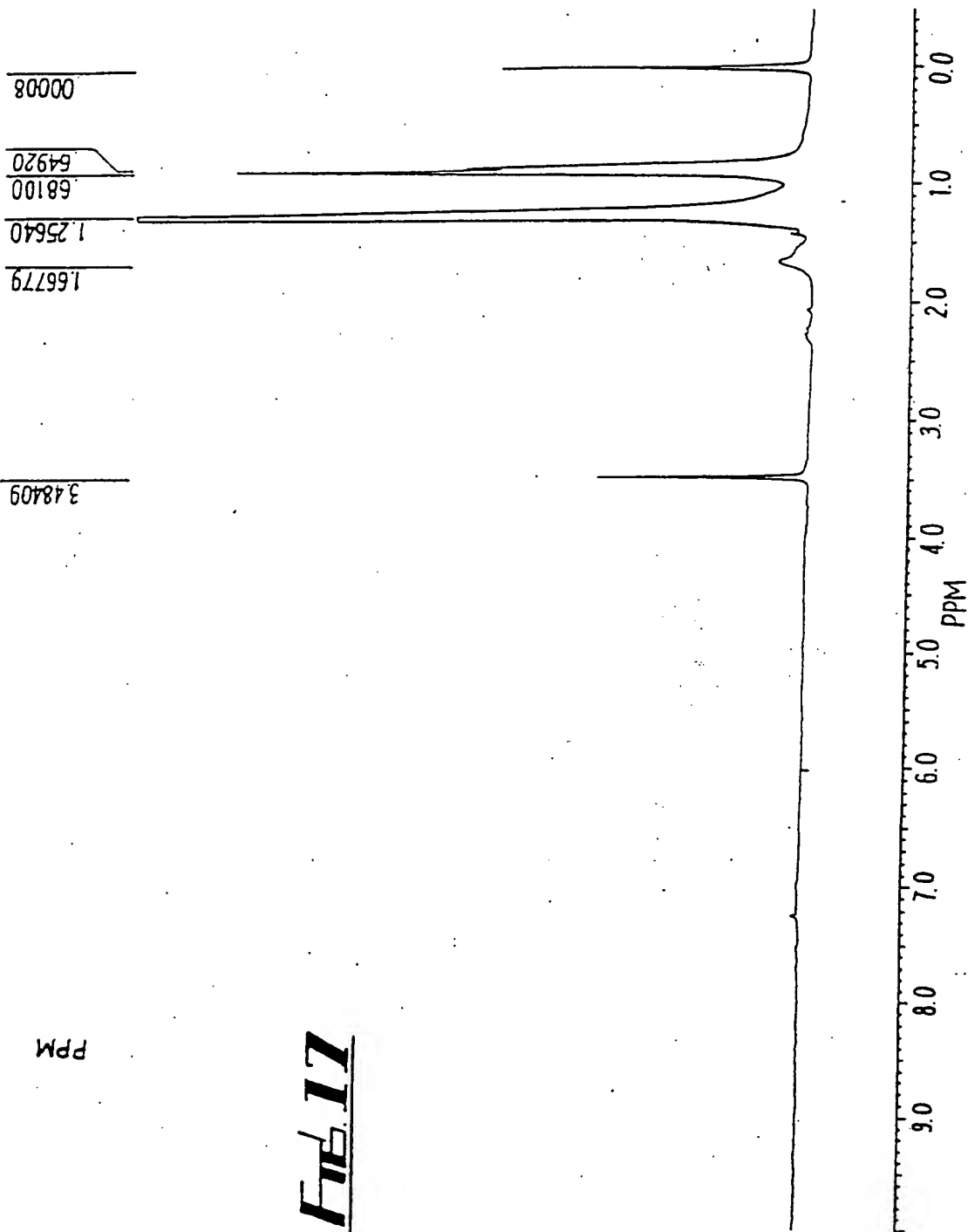


FIG. 16

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**Fig. 17**

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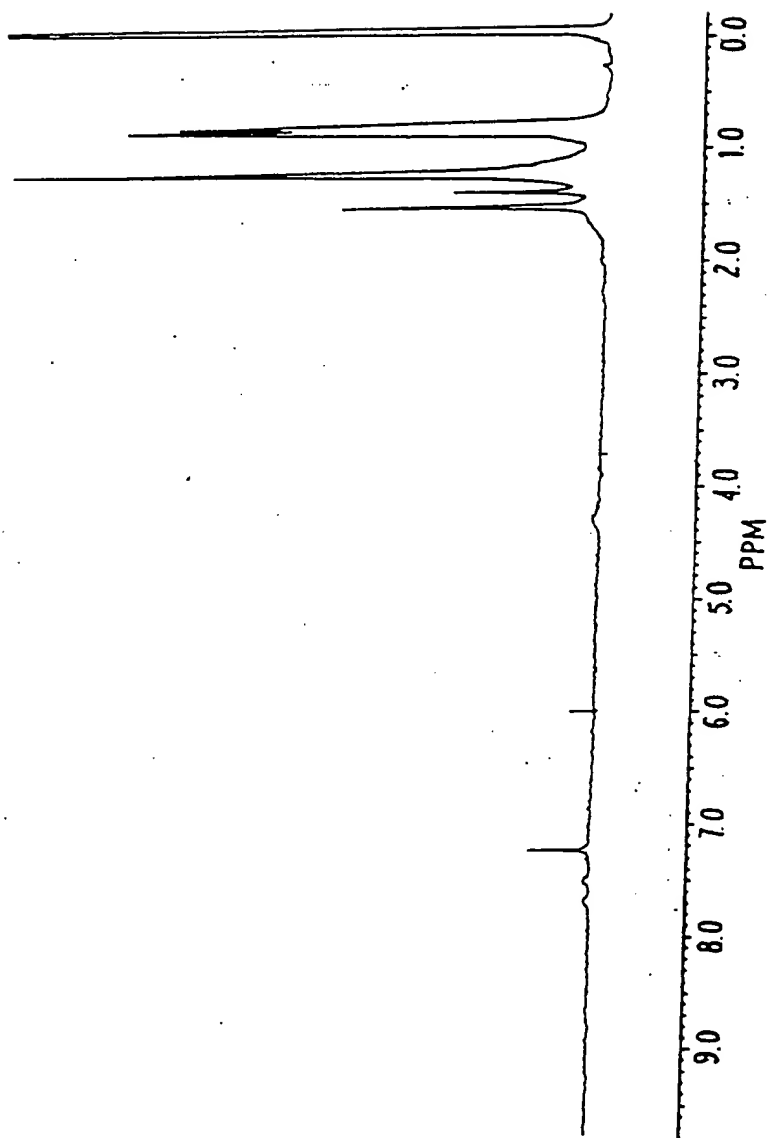
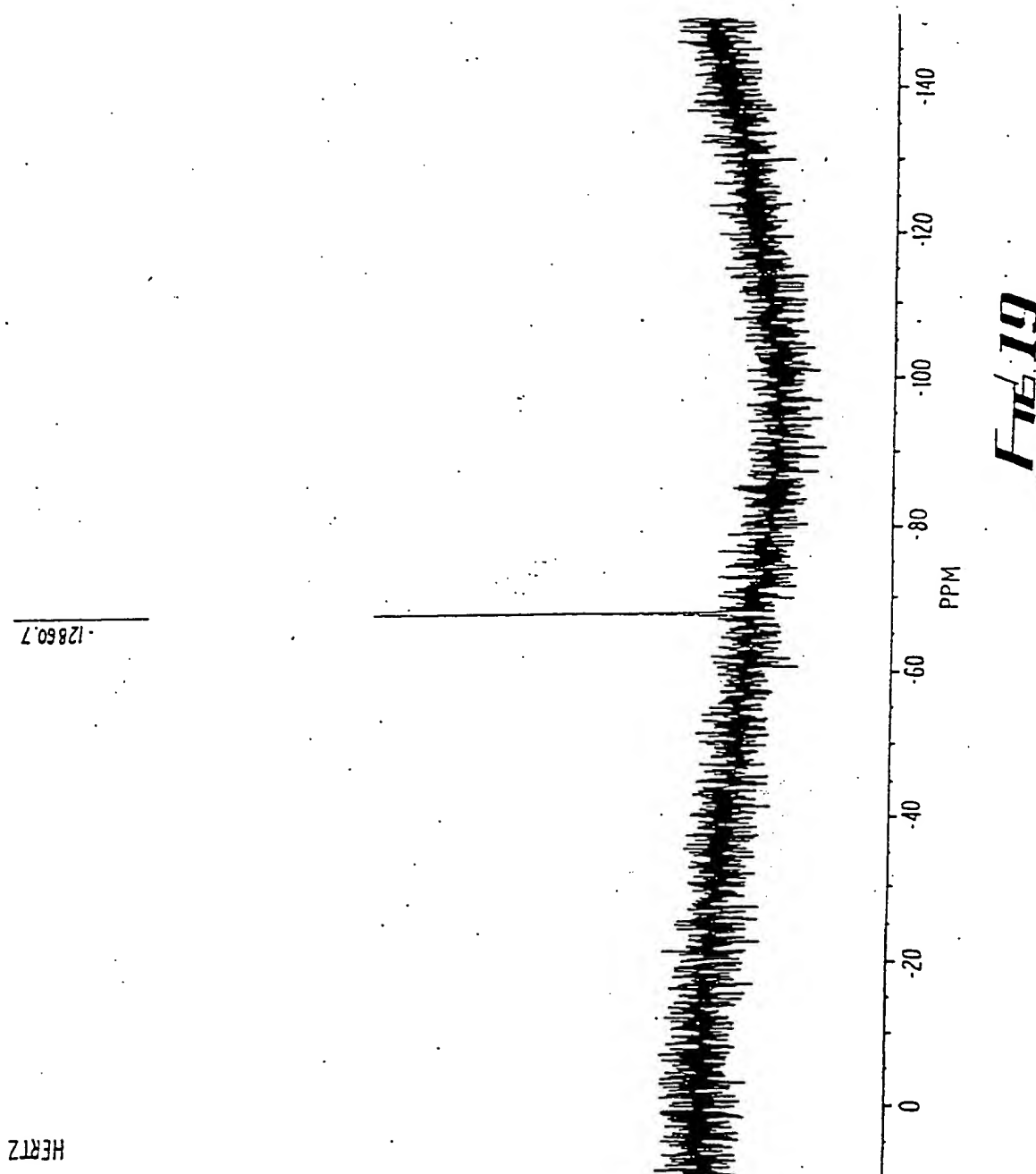
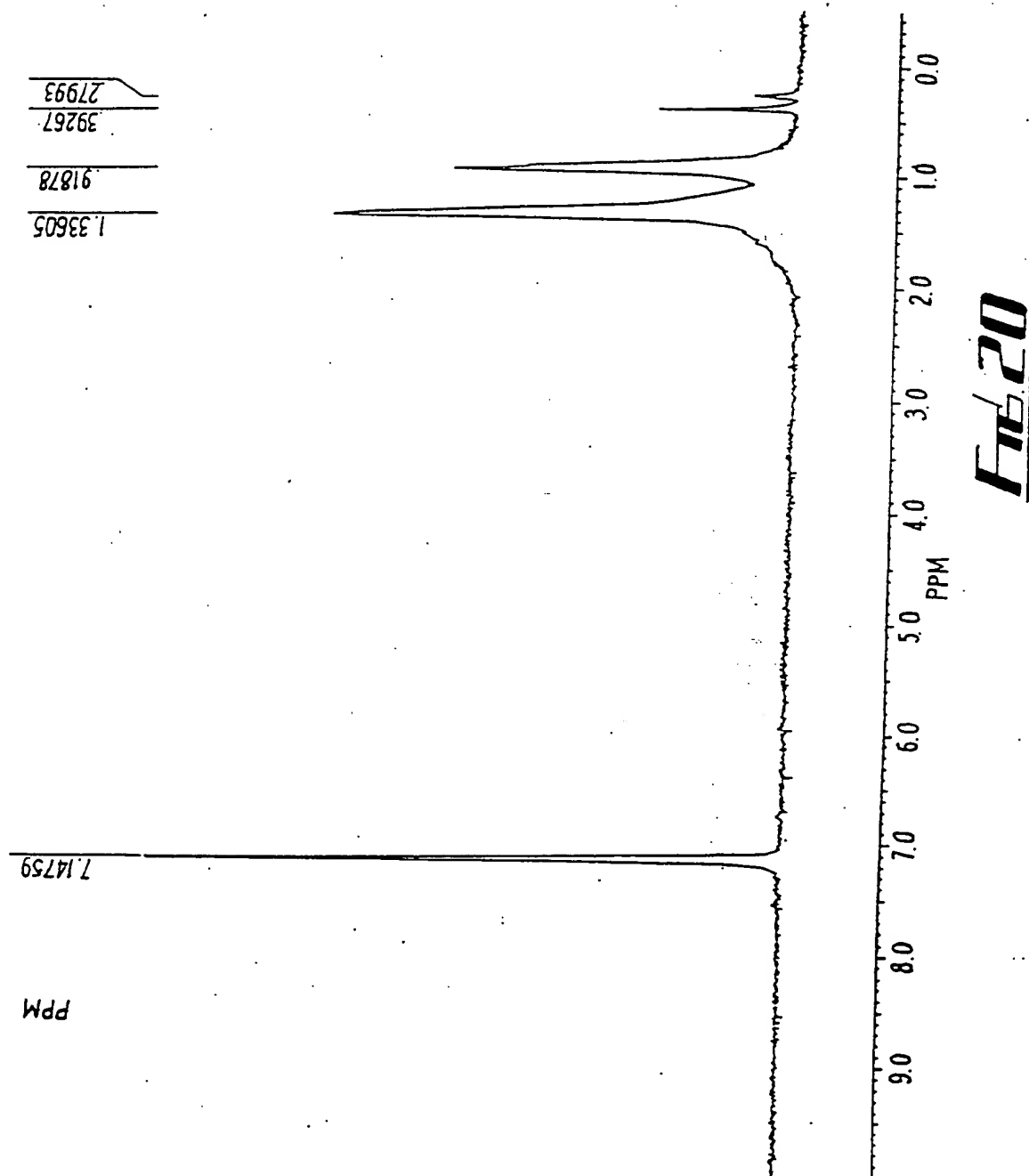


Fig 18

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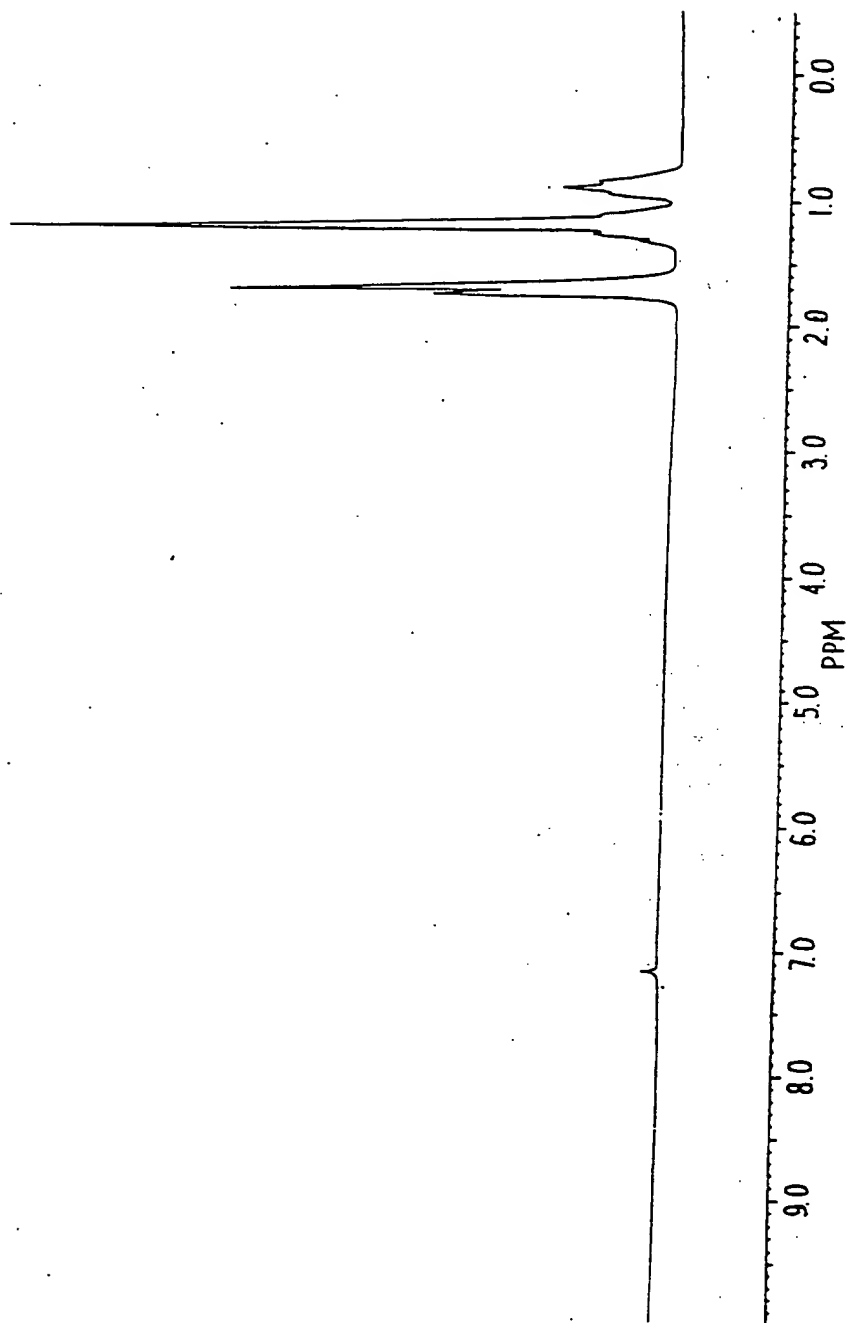
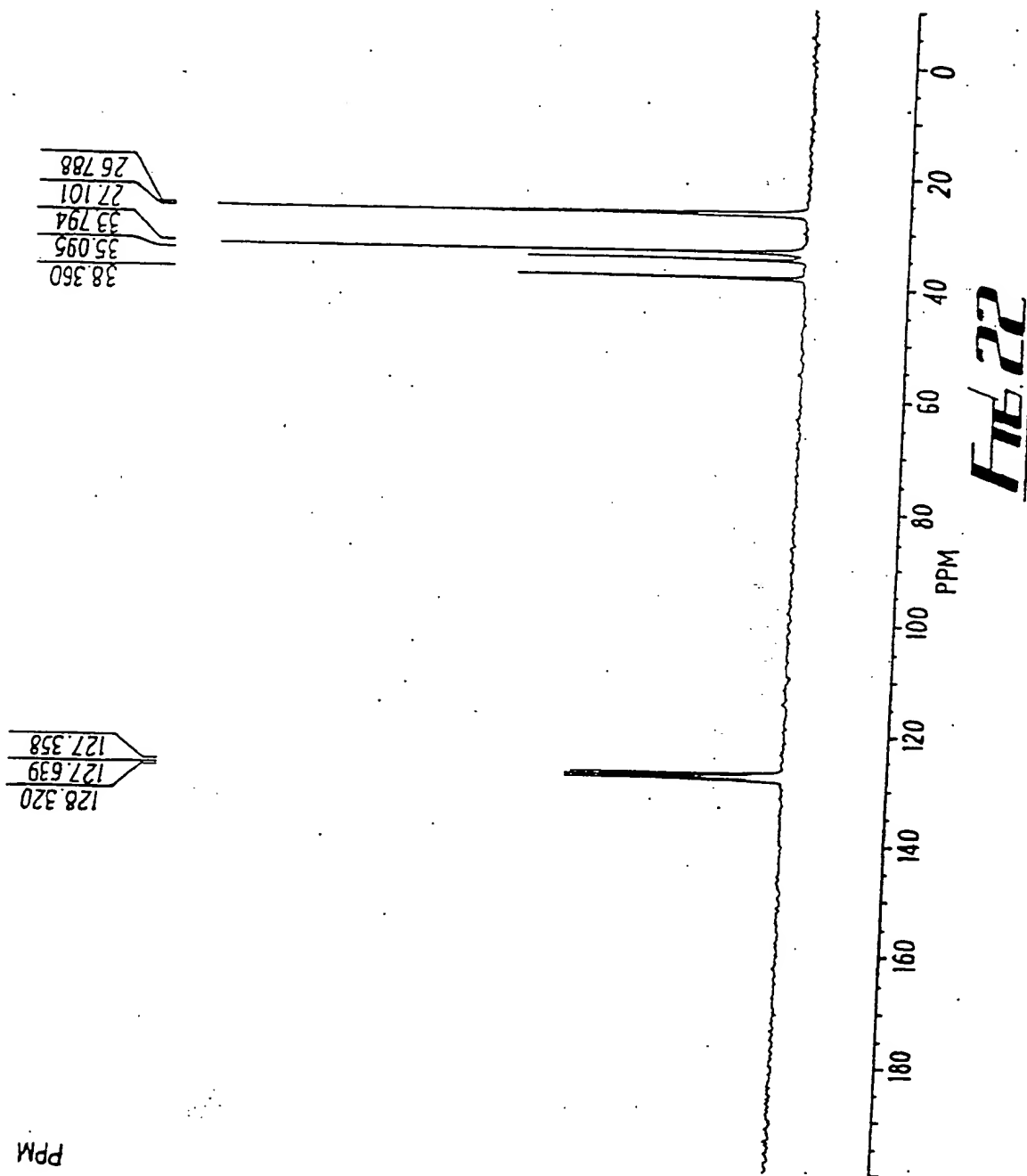


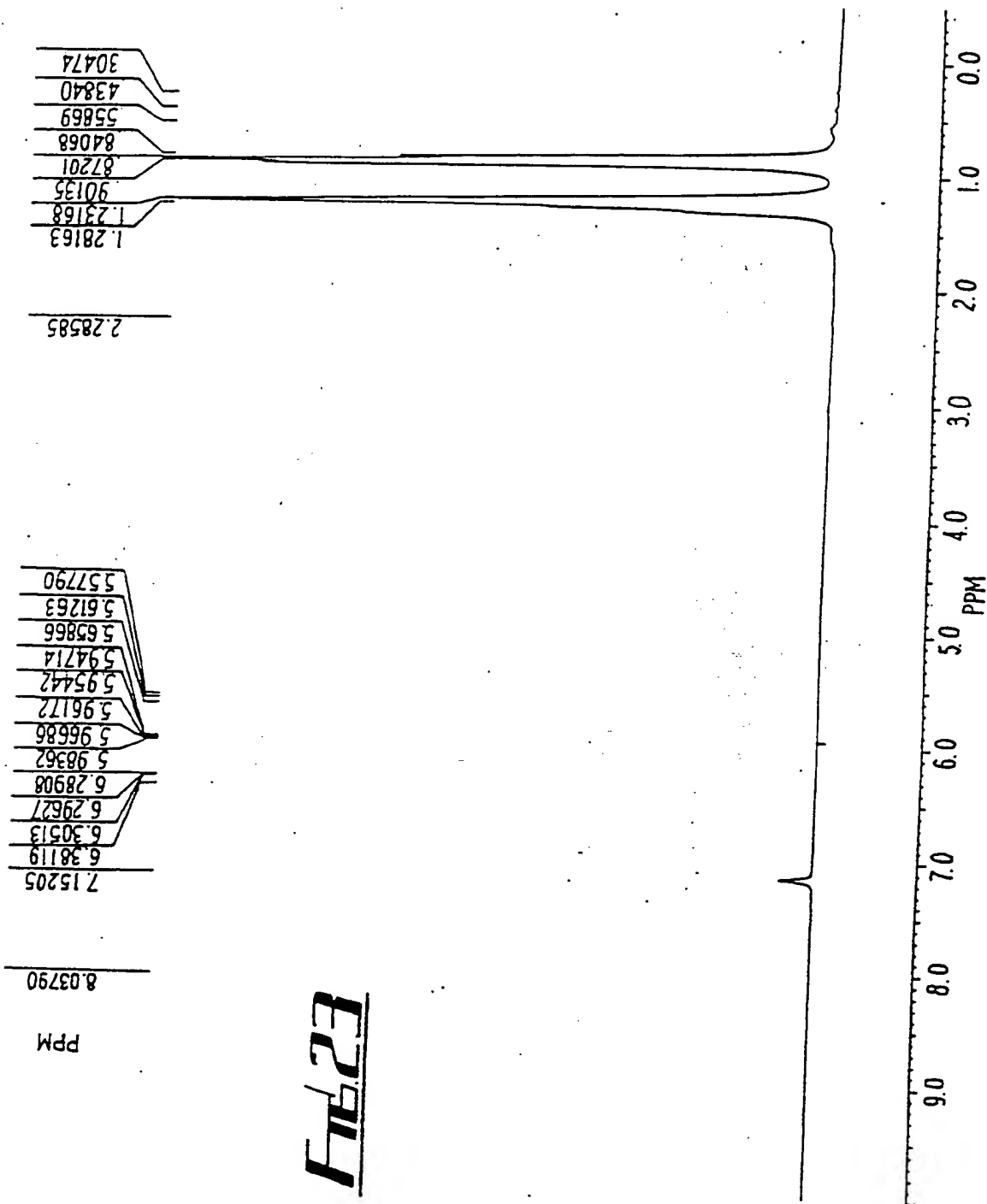
Fig 21



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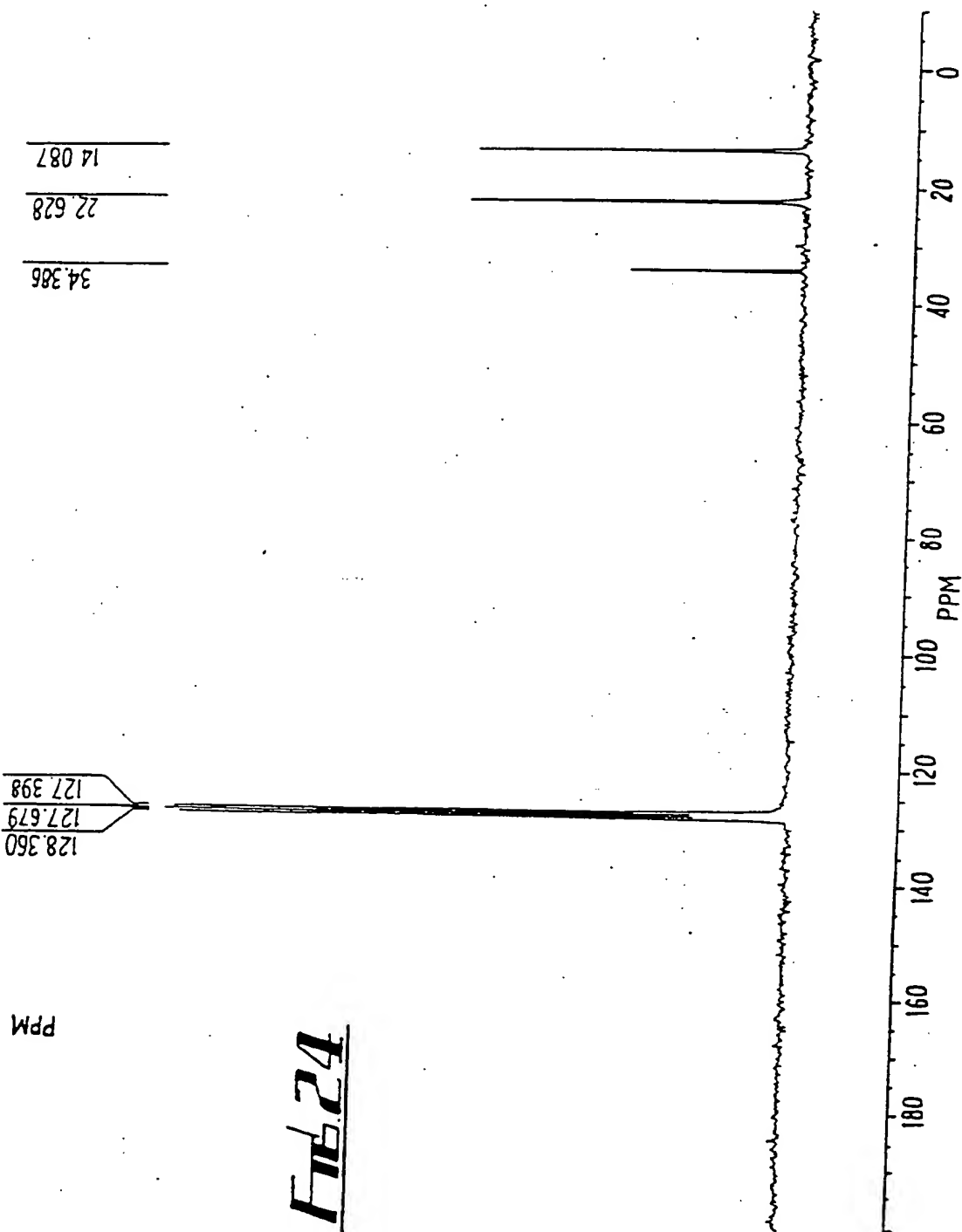


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**Fig 23**

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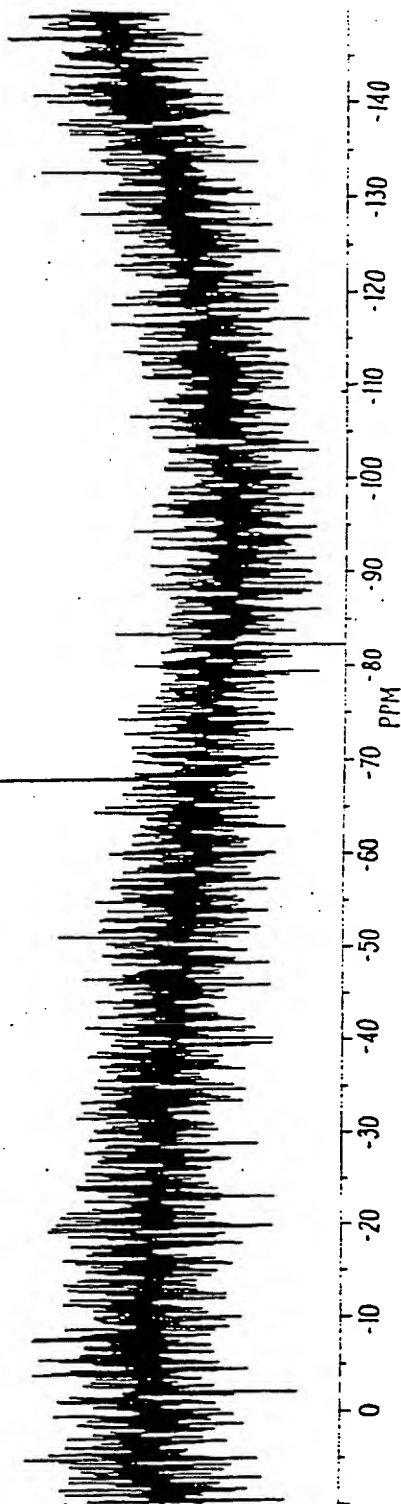


Fig 25

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 93/02391

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 G03F7/004 C23C16/18 H01L21/285 G03F1/08 G03F7/16  
G03F7/20 C07F1/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 G03F C23C H01L C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
2 X	WO,A,90 02827 (HUGHES AIRCRAFT COMPANY) 22 March 1990  see page 8, line 28 - line 36 see page 4, line 13 - line 28	1,2,4; 9-11,16, 18
Y	see page 5, line 1 - line 8 see page 6, line 5 - line 8 see page 10, line 35 - line 36 ---	3,5
3 X	RESEARCH DISCLOSURE 10 March 1992 , HAVANT, UK page 211 XP000301117 ANONYMOUS 'Pin Repair of MLC Substrate I / O Pads by Focused Ion Beam Techniques' * third paragraph * --- -/--	1,2,4, 9-11,16, 18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 February 1994

Date of mailing of the international search report

16.03.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/02391

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 714 627 (R.J. PUDDEPHATT ET AL.) 22 December 1987  see column 1, line 8 - line 15 see column 2, line 24 - line 35	1,2, 4-11,13, 16-18
Y	see column 6, line 68  ---	3
X	T. MOLE, E.A. JEFFERY 'ORGANOALUMINIUM COMPOUNDS' 1972, ELSEVIER PUBLISHING COMPANY, AMSTERDAM, THE NETHERLANDS see page 34  ---	19
X	US,A,5 104 684 (T.TAO ET AL.) 14 April 1992 see column 2, line 13 - line 15 see column 4, line 28 - line 35 see column 4, line 49 - line 68; claims 1,4,6,7  ---	12,13
Y	WO,A,90 06315 (MERCK GMBH) 14 June 1990 see page 14, line 9 - line 16  -----	5

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Information on patent family members

International Application No

PCT/GB 93/02391

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US-A-4714627	22-12-87	CA-A- 1250309	21-02-89
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